91602
new 82-10

ontario hydro
research division

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research If
Reproduced in Whole or in Part

COLLECTION, CONDITIONING, IMMOBILIZATION AND ENCAPSULATION OF THE AIRBORNE RADIOACTIVE NUCLIDES FROM A CANDU FUEL REPROCESSING PLANT

S-D. Chang
Process Chemistry Section
Chemical Research Department
Report No 87-44-K

ABSTRACT

Irradiated fuel from CANDU stations contains depleted uranium, plutonium, and waste fission products. Separation of the fissile plutonium would provide a valuable energy resource. Several processes are available for reprocessing of irradiated fuel, ie, the Purex process, the Amine process, and TBP co-processing. Regardless of the process selected, the head-end operations are the same: mechanical fuel disassembly, shearing, and fuel dissolution. These operations result in two off-gas streams, the head-end off-gas (HOG) and the dissolver off-gas (DOG), which contain radionuclides such as iodine-129, carbon-14, krypton-85, and tritium. This report consists of an evaluation and selection of treatment processes for collection and immobilization of the gaseous radionuclides, with flowsheets, and mass and energy balances for the selected processes.

job	file	date	report no.
31-573-061	837.245	July 8, 1987	87-44-K

91602
new 82-10

ontario hydro
research division

EXECUTIVE SUMMARY

S.-D. Chang
Process Chemistry Section
Chemical Research Department

Irradiated fuel from CANDU nuclear power stations contains depleted uranium, plutonium, and waste fission products. Ontario Hydro presently stores irradiated fuel under water in storage bays at nuclear generating stations. Separation of the fissile plutonium would provide a valuable energy resource which could be recycled in nuclear fuel. A final decision has not been made on the disposition of irradiated nuclear fuel. To provide a sound technical basis for this decision, Ontario Hydro has supported and assisted AECL in research programs aimed at either reprocessing of the fuel, recovery of the fissile material, and disposal of the waste or developing a method for permanent disposal of this irradiated fuel.

Several processes could be used for reprocessing of irradiated CANDU fuel, ie, the Purex process, the Amine Process, and TBP co-processing. Regardless of the option selected, the head-end operations are the same: mechanical fuel disassembly, shearing, and fuel dissolution. These operations result in two off-gas streams, the head-end off-gas (HOG) and the dissolver off-gas (DOG), which contain radionuclides such as iodine-129, carbon-14, krypton-85, and tritium. Two options are available for fuel dissolution. One is direct dissolution and the other is voloxidation. In direct dissolution, the fuel is dissolved in nitric acid immediately after shearing. This results in the release of most of the first three radionuclides into the off-gas but all of the available tritium is retained within the dissolver nitric acid. Subsequent removal of this tritium is a complex and expensive operation. Some tritium, fixed in the metallic matrix and unavailable for dissolution, will remain with the cladding hull.

job	file	date	report no.
31-573-061	837.245	July 8, 1987	87-44-K

In voloxidation, the process involves oxidizing the sheared fuel in air up to 600°C thus causing the UO_2 fuel matrix to expand, disintegrate into a fine U_3O_8 powder, and separate from the cladding. It is assumed that all available tritium is released from the fuel in the oxidized form and that varying fractions of the other gaseous radionuclides will also be released during the voloxidation step. Thus, tritium can be trapped before its dispersion into the dissolver liquid.

As part of Ontario Hydro's Recycle Assistance Program in support of AECL Fuel Recycle R&D, the Chemical Research Department undertook a conceptual design of an off-gas treatment process for CANDU fuel reprocessing plants, with and without thermal pretreatment of the fuel (voloxidation). The project originally consisted of the four tasks listed below; the first two were to be carried out by the Process Development Unit of the Chemical Research Department and the latter two were to be carried out by Nuclear Materials Management Department. At a review later the Chemical Research Process Development Unit was asked to include within the conceptual designs, processes for immobilization of the gaseous radionuclides.

Tasks:

1. Selection of treatment processes for the collection of the various radionuclides of concern and preparation of flow sheets.

2. Preparation of mass and energy balances for each off-gas treatment flow sheet selected.

3. Selection and sizing of process equipment.

4. Preparation of cost estimates for selected options.

This report is the documentation of Tasks 1/2 and the immobilization of the gaseous radionuclides. Tasks 3/4 were reported elsewhere by Nuclear Materials Management Department, Design & Development Division.

At the end of this report the following conclusions are presented:

The technology for collecting individual radionuclides is available and can be chosen to match the preset selection criteria: to be simple, reliable, effective, safe, and economic.

Both front-end dissolution processes, direct dissolution and voloxidation, seem effective. The choice will depend on economics. In accordance with the recent analysis by NMMD, the capital cost for the direct dissolution process is far greater than that of the voloxidation process. The conclusion was that future work related to CANDU fuel reprocessing should focus on voloxidation.

A drying process based on molecular sieves is a good technique for trapping tritiated moisture. For immobilization, tritiated waste solidification in cement and gypsum mixture is recommended. The cement paste can be cast in a 100 L polyethylene drum, the primary container, then placed into a 115 L asphalt-lined steel drum for dry storage. Prior to the waste conditioning a volume reduction through ELEX or CECE process is highly desirable and recommended.

Absorption of iodine on silver-doped solid sorbent, specifically silver nitrate on alumina or silver nitrate on silica, is a good choice because of their high efficiency and freedom from poisoning from NO_x and H_2O. The high stability of the product with respect to heat and insolubility in water render it suitable for direct disposal. Silver iodide in cement is the preferred form for storage or disposal of the iodine-129. Recovery of silver is not recommended because the leaching resistance of the final product, eg, lead iodide, has not been established.

The $Ca(OH)_2$ solid bed was selected for absorption of carbon-14 dioxide as the product $CaCO_3$ is a chosen form for further conditioning. The used solid bed in a sealed canister can be encapsulated in a concrete matrix and a carbon steel outer container to act as a mould and to provide protection to the waste form during transport and storage. The alternative would be to extract the carbon-14 for commercial use if it is warranted by the market. The choice between the two alternatives depends upon the economic merit.

The selective absorption of noble gases in fluorohydrocarbons at low temperature and pressures is the choice for trapping krypton-85 and xenon as it provides a high purity product and maintains a low krypton inventory. It is recommended that krypton be immobilized and encapsulated through the chemifixation process into zeolite 5A. The autoclave employed for the fixation serves as the secondary containment for storage in an underground vault.

The processes selected above have been integrated successfully on paper to maintain the system pressure low to minimize the release of radioactive nuclides. Since the process is not yet proven it must be tested in the laboratory before it is scaled up for commercial applications.

TABLE OF CONTENTS

		Page
1.0	INTRODUCTION	1
2.0	PROCESS SELECTION	2
	2.1 Process Selection Criteria	3
	2.2 Dissolution Processes	3
	2.3 Iodine Absorption	3
	2.4 Carbon-14 Removal	4
	2.5 Noble Gases Removal	5
	2.6 Options for Tritium Removal	6
3.0	CONCEPTUAL PROCESS DESIGN	7
	3.1 General Description	7
	3.2 Design Basis	7
4.0	MATERIAL BALANCES AND FLOW DIAGRAMS	8
	4.1 Direct Dissolution Process	8
	4.2 Voloxidation Process	9
	4.3 Off-Gas Tail End Process	10
	4.4 Combined Electrolysis/Catalytic Exchange	11
5.0	WASTE CONDITIONING	12
	5.1 Tritiated Waste	12
	5.2 Iodine-129	14
	5.3 Carbon-14	15
	5.4 Krypton-85	15
6.0	CONCLUSIONS	16
7.0	REFERENCES	17
8.0	ACKNOWLEDGMENTS	20
9.0	APPENDIX	31

LIST OF TABLES

Table		Page
1	Comparison of Voloxidation and Direct Dissolution	21
2	Distribution of Volatile Radioactive Nuclide in 5000 kg Fuel	22
3	Summary of Waste Conditioning for Storage	23

LIST OF FIGURES

Figure		Page
1	Off-Gas Front End Processes	24
2	Off-Gas Tail End Process	25
3	Material Balance for Off-Gas With Direct Dissolution Process	26/27
4	Material Balance for Off-Gas System With Voloxidation	28/29
5	Combined Electrolysis/Catalytic Exchange (CECE) Process for Detritiation of Water	30

91601
new 82-10

ontario hydro
research division

To: Dr. D. Mills
Director of Research

COLLECTION, CONDITIONING, IMMOBILIZATION AND ENCAPSULATION OF THE AIRBORNE RADIOACTIVE NUCLIDES FROM A CANDU FUEL REPROCESSING PLANT

S-D. Chang

1.0 INTRODUCTION

Irradiated fuel from CANDU nuclear power stations contains depleted uranium, plutonium, and waste fission products. Ontario Hydro presently stores irradiated fuel under water in storage bays at nuclear generating stations. Separation of the fissile plutonium would provide a valuable energy resource which could be recycled in nuclear fuel. A final decision has not been made on the disposition of irradiated nuclear fuel. To provide a sound technical basis for this decision, Ontario Hydro has supported and assisted AECL in research programs aimed at developing a method for either reprocessing of the fuel, recovery of the fissile material, and disposal of the waste or the permanent disposal of this irradiated fuel.

Several processes have been considered for reprocessing of CANDU irradiated fuel, ie, the Purex process, the Amine process, and TBP co-processing. Regardless of the option selected, the head-end operations are the same: mechanical fuel disassembly, shearing, and fuel dissolution. These operations result in two off-gas streams, the head-end off-gas (HOG) and the dissolver off-gas (DOG), which contain radionuclides such as iodine-129, carbon-14, krypton-85, and tritium. In direct dissolution, the fuel is dissolved in nitric acid immediately after shearing. This results in the release of most of the first three radionuclides into the off-gas but all of the available tritium is retained within the dissolver nitric acid. Subsequent removal of this tritium is a complex and expensive operation. Some tritium fixed in the metallic matrix and unavailable for dissolution, will remain with the cladding hull.

To prevent oxidation and dissolution of the available tritium in the dissolver liquid it has been proposed by AECL that the sheared fuel be preheated prior to being dissolved in nitric acid. This process, known as voloxidation, involves oxidizing the sheared fuel in air up to 600°C thus causing the UO_2 fuel matrix to expand, disintegrate into a fine U_3O_8 powder, and separate from the cladding. It is assumed that all available tritium is released from the fuel in the oxidized form and that varying fractions of the other gaseous radionuclides will also be released during the voloxidation step.

In 1985, as part of Ontario Hydro's Recycle Assistance Program in support of AECL Fuel Recycle R&D, the Chemical Research Department undertook a conceptual design of an off-gas treatment process for CANDU fuel reprocessing plants, with and without thermal pretreatment of the fuel (voloxidation). The project originally consisted of the four tests listed below; the first two were to be carried out by the Process Development Unit of the Chemical Research Department and the latter two were to be carried out by Nuclear Materials Management Department.

Tasks:

1. Selection of treatment processes for the collection of the various radionuclides of concern and preparation of flow sheets.

2. Preparation of mass and energy balances for each off-gas treatment flow sheet selected.

3. Selection and sizing of process equipment.

4. Preparation of cost estimates for selected options.

At a later date the Process Development Unit was asked to include within the conceptual designs, processes for immobilization of the gaseous radionuclides which were present in the off-gas.

Tasks 1 and 2, as originally defined, were completed in the last quarter of 1985 and the information was supplied to Nuclear Materials Management Department in the form of a brief write-up, flow sheets, and tables of mass and energy balances for each option. This information has now been incorporated into Nuclear Materials Management Report 85420, Off-Gas System for a CANDU Fuel Reprocessing Plant-Engineering and Cost Analysis, May 1986. With the permission of NMMD, a portion of that report, specifically the design description, has been reproduced here with little or no change as this was based on the information supplied by the Chemical Research Department.

To provide the background to the NMMD report, this report describes the rationale on which the selected treatment processes were chosen and the calculations on which the mass and energy balances which were supplied to NMMD were based. In addition, this report includes a description of processes for the conditioning, immobilization, and encapsulation of the collected gaseous radionuclides from a CANDU fuel reprocessing plant.

2.0 PROCESS SELECTION

The technology for reprocessing plant off-gas clean-up has been developed for some time in several countries through their nuclear weapons programs and through their breeder reactor programs. Without defined scope and criteria, it is difficult to select a set of processes and integrate them for off-gas treatment. In this section the scope of the off-gas treatment is defined and the selection criteria for individual processes are discussed.

Many airborne radioactive elements will be released from the fuel during reprocessing. Many semivolatile components will be trapped by the filters. Therefore, only volatile components with long half-lives such as I-129 and C-14

and/or with high activity such as H-3 and Kr-85 are considered in the present off-gas treatment study.

2.1 Process Selection Criteria

The process to be selected must be simple and the components removed from the off-gas should be either recycled or conditioned for storage and disposal. The process should not produce additional waste streams or create a difficult disposal problem. The process selected must be reliable since it must be remotely operated and controlled. Downtime must be kept to a minimum. It must be effective in the separation of radioactive components from non-radioactive gases to achieve the desired decontamination factors. The process selected must also satisfy the ALARA principle. For safety considerations, the process selected must not accumulate a substantial amount of radioactivity, ie, it must have a low inventory of radionuclides.

2.2 Dissolution Processes

Two dissolution process options: direct dissolution and voloxidation followed by dissolution of the powdered fuel matrix, were considered in this study. In the direct dissolution process the chopped or sheared fuel is dissolved directly in nitric acid in which uranium dioxide and the available tritium are oxidized. Therefore, the available tritium, now in oxidized form, will disperse into the solution from which it is difficult to recover. In the voloxidation process uranium dioxide and the available tritium are oxidized prior to the dissolution process. The tritium in the gaseous oxidized form is removed before dissolution and can be recovered simply through a gas drying process.

A comparison of these two options is shown in Table 1. It can be seen that one key difference in the two processes is the method of tritium recovery. In the direct dissolution process tritium, as HTO, is recovered from very dilute tritiated waste water; in the voloxidation process the tritium in the form of gaseous HTO is trapped by a drying process. Another key difference is in the UO_2 oxidation step. In the direct dissolution process, HNO_3 is used in the liquid phase while in the voloxidation process, oxygen is used in the gas phase. The other differences are included in Table 1 and will be discussed in later sections.

2.3 Iodine Absorption

Iodine isotopes, particularly I-129, have historically received close attention because they are concentrated in the thyroid gland and have serious biological consequences. This species requires the highest overall decontamination factor of all off-gas components. For example, in the Federal Republic of Germany the retention requirements for radioiodine are 99.99% and 99% for elemental iodine and organic iodine respectively/1/. In Canada, the newest nuclear station, Darlington NGS, specifies 99.99% and 99.8% retention for the same elemental radioiodine and organic radioiodine respectively/2/.

Methods of iodine removal considered were:

(a) Alkaline scrubbing;

(b) Activated carbon sorbents loaded with KOH and tri-substituted amine;

(c) The Mercurex process;

(d) The Iodox process;

(e) Absorption on silver-doped solid sorbents.

The last process was chosen because it has several advantages over the other iodine removal processes, including:

(a) Absence of a fire hazard;

(b) Good capability to retain iodine under varying temperature conditions;

(c) High efficiency in humid conditions;

(d) High stability and insolubility (in water) of the loaded sorbent render it suitable for direct disposal;

(e) Complexity of liquid scrubbing is avoided;

(f) The replacement of sorbent cartridges can be easily adapted to remote handling.

There are various types of silver-impregnated solid sorbents available such as silver zeolite, silver mordenite, silver alumina, and silver silica. The iodine absorption capacity of the first two is somewhat affected by the presence of NO_x and H_2O, while that of the latter two is not/3/. Therefore, silver alumina or silver silica are recommended in this study.

The disadvantage of all silver-loaded sorbents is their high cost, due to the silver content. However, silver alumina and silver silica are less costly than silver-loaded zeolite and mordenite due to a lower silver content. The possibility of regeneration may offset the high cost in the future, but the waste in silver iodide form is much more stable than that of lead iodide -- the regeneration product. Regeneration is, therefore, not recommended.

Extensive testing of the iodine removal effectiveness of silver-loaded sorbents has been carried out in the United States, Germany and Japan, and successful pilot plant and in-plant testing has been performed. Iodine decontamination factors of greater than 10^3 have been achieved/4/.

2.4 Carbon-14 Removal

Carbon-14 is produced mainly by neutron interactions with ^{14}N, ^{15}N, ^{16}O, ^{17}O, or ^{13}C which are present in the fuel, the cladding, and the primary cooling system. Carbon-14 has been identified as a potential health hazard due to the ease with which it may be assimilated into the biosphere and its long half-life of 5736 years.

During fuel reprocessing, carbon-14 evolves mainly as carbon-14 dioxide. Capture of CO_2 is, therefore, necessary to prevent carbon-14 from being released to the biosphere. There are many carbon dioxide fixation and removal processes: physical absorption of CO_2 in amine solution, physical adsorption of CO_2 on a molecular sieve, and chemical reaction with NaOH/5/. Most of them, however, do not fix the carbon dioxide in a form suitable for final disposal. A method that

generates, by a gas/solid reaction, a waste form suitable for final disposal is highly desirable. Two candidates: $Ba(OH)_2$ and $Ca(OH)_2$, have been widely suggested as solid beds for fixation of the dilute CO_2 from an off-gas stream, as they possess excellent resistance to leaching.

Despite its many advantages, calcium hydroxide was rejected earlier because the product $CaCO_3$ could form a layer over the $Ca(OH)_2$ resulting in severe diffusional limitations for $C^{14}O_2$ absorption at ambient conditions/5/. However, recent Ontario Hydro studies/6,7/ revealed that at high humidity, the reaction rate is chemically controlled and only at low humidities is the reaction rate limited by diffusion through the carbonate layer. The moisture apparently lowers the resistance to diffusion through the carbonate layer formed by the reaction/7/. Therefore, a calcium hydroxide bed was chosen in this work as high humidities can be maintained in the off gases.

The advantages of this method are:

(a) the process is simple, reliable, safe, and operates at ambient temperature and pressure;

(b) $Ca(OH)_2$ used in the process is inexpensive, non-toxic, and thermally stable;

(c) carbon-14 is fixed in a stable solid form suitable for disposal;

(d) $Ca(OH)_2$ utilization is high (about 80 percent) at high humidity; and

(e) high decontamination factors (greater than 20) are achievable.

To date, the ambient temperature calcium hydroxide sorbent system has been studied only on the pilot scale and with non-radioactive CO_2. A full scale demonstration unit to remove carbon-14 dioxide from the moderator cover gas of NPD-NGS, however, has been built.

2.5 Noble Gases Removal

Krypton-85 and stable xenon isotopes are present in CANDU irradiated fuel. Although krypton is present only in a small fraction, it contributes the largest portion of radioactivty to the off-gas. Separation of krypton from the non-radioactive xenon is also necessary to reduce the waste volume and to recover non-radioactive xenon for commercial use.

The concentration of the noble gases in the off-gas stream will be closely related to the fuel burn-up, the dissolver operation, and the design sparge rate of air. If voloxidation is employed, a fractional amount of Kr-85 (7-17%) will be released directly to the HOG prior to fuel dissolution/4,8/.

Presently, the United States is the only nation to have established emission limits for Kr-85/4/. The practice of other nations is to vent krypton and xenon from reprocessing plants directly to the atmosphere.

Three krypton (and xenon) capture methods were evaluated:

(a) inorganic solid bed adsorption;

(b) cryogenic distillation; and

(c) the fluorocarbon selective absorption process.

Only the latter two are near commercial availability and they were, therefore, evaluated. Cryogenic distillation is a well developed technology, but this process requires a high level of feed preparation and has a very high krypton inventory. Hence, the fluorocarbon absorption method was chosen because:

(a) it is a well developed technology close to commercial scale operation;

(b) it provides a high purity product and maintains a low krypton inventory;

(c) recent German developments/9/ allow operation at low pressures (a desirable feature for safety considerations); and

(d) the capital and operating costs may be lower compared to the cryogenic distillation process.

The fluorocarbon absorption process has been extensively studied and developed at Oak Ridge on a pilot plant scale for more than 1 year. Extensive pilot-scale studies are also being carried out at Karlsruhe, Germany/9,10,11/.

Prior to feeding the off-gas to the noble gas removal process, the oxygen and moisture in the gas must be removed. The oxygen can be eliminated through an oxygen recombiner in which any free oxygen is reduced to H_2O by reaction with hydrogen. This eliminates the formation of ozone downstream in the fluorocarbon absorption process. Also, any NO_2 that enters is reduced to N_2O and NO.

Because the reduction of oxygen (and NO_2) with hydrogen is exothermic and the catalyst materials are adversely affected by excessive high temperatures, the cooling cycle must be effective. The AECL Waterproof Catalytic Recombiner, using water as the coolant, has been chosen.

The moisture in the off-gas must also be removed so that it will not freeze in the noble gas separation process. For removing moisture, a molecular sieve drier was chosen.

2.6 Options for Tritium Removal

Tritium is present in irradiated fuel as a tertiary fission product. The majority of tritium may diffuse into the Zircaloy cladding and form zirconium tritide which would most likely stay with the Zircaloy hull through the reprocessing operations. The remaining portion in the forms of HT/HTO, T_2/T_2O, and/or DT/DTO will be released from the fuel in gaseous form if the voloxidation process is employed and in the dissolver liquid stream if a direct dissolution process is adopted.

The removal of tritium from a dilute aqueous stream, although possible, is a very difficult task, especially when the stream contains highly radioactive nuclides. The preferred method is to remove it before its dispersion. In the voloxidation process, volatile tritium components will be released together with other volatile and semi-volatile components from the spent fuel before its dissolution. In the presence of oxygen at high temperatures all tritiated gas, HT, T_2, or DT, will be converted into HTO, T_2O, or DTO respectively which can be

trapped readily in molecular sieve dryers. If direct dissolution instead of voloxidation is chosen, the tritium removal system must include a hydrogen/water exchange process, an electrolysis process, or a combined electrolysis and catalytic exchange process (CECE).

The CECE is an isotopic enrichment process for the separation of tritium as HTO from aqueous effluents. It is a combination of water electrolysis and tritium exchange between hydrogen and water, the exchange being promoted by a hydrophobic catalyst. The process is thus based on two significant isotopic effects: the kinetic isotope effect in the electrolytic hydrogen evolution reaction, and the equilibrium isotope effect in the tritium exchange reaction between hydrogen gas and liquid water. Both isotope effects favour concentration of tritium in the liquid phase relative to the gaseous phase and thus the tritiated water is concentrated. The electrolysis process is also effective; however, it is less efficient in energy utilization than the CECE process.

3.0 CONCEPTUAL PROCESS DESIGN

3.1 General Process Description

An off-gas process begins with fuel chopping and/or heating and oxidation operations. Air is introduced at the beginning of the process to serve as a carrier gas. This gas which is essentially air carrying radionuclides released from the chopping and oxidation operation is called "head-end off-gas" (HOG). The chopped/heated fuel dissolving in nitric acid will result in some gas being liberated from the solution. This gas carried by air is termed "dissolver off-gas" (DOG). The droplet and mist carried by DOG as well as particulate carried by HOG must be removed to complete the front-end off-gas process. As shown in Figure 1, the top portion is the block diagram for the direct dissolution process; the bottom portion is the voloxidation process. It may be seen that HTO is recovered from the waste water in the direct dissolution process and the same is, however, recovered from gas in the voloxidation process.

The HOG and the DOG are then pumped downstream for further separation. The compressor employed in pumping gas also maintains the front-end process slightly below atmospheric pressure such that the activity of radionuclides can be contained within the process equipment.

The tail-end process involves iodine removal, carbon-14 dioxide fixation, and noble gas separation. As shown in Figure 2, no matter whether a direct dissolution or voloxidation is chosen for the front end, the tail-end process is the same for both options.

3.2 Design Basis

It is assumed in this study that 5000 kg/d of heavy metal (irradiated uranium in fuel) is to be reprocessed. This irradiated fuel will have been cooled for five to ten years. In the voloxidation process it is assumed that all iodine-129, carbon-14, krypton-85, and xenon and all available tritium are released to the head-end off-gas/12/. In the direct dissolution process only portions of them are released to the head-end off-gas. The inventory of these radioactive nuclides in 5000 kg of fuel is listed in Table 2/12,13/. The fractions of each radioactive nuclide released to the head-end gas also are

included. About 1% of the cesium and ruthenium inventory are released but trapped before entering the head-end off-gas. Air is employed to carry the off-gas at the rate of 978 Nm^3/d or 196 Nm^3/tHM. In addition, 235 Nm^3/d^* of oxygen is used for uranium oxidation in the voloxidation process or for NO_x recovery in the direct dissolution process.

4.0 MATERIAL BALANCES AND FLOW DIAGRAMS

Details of the material balance development are given in Appendix A and Appendix B. Only flow diagrams and the result of the mass balances are discussed in this section.

4.1 Direct Dissolution Process

The flow diagram and mass balances for the direct dissolution option are shown in Figure 3. Stream numbers shown in Figure 3 are referred to in this section. In direct dissolution, the fuel (Stream 5) is dissolved in nitric acid directly after fuel shearing. In this case, the UO_2 is oxidized to U_3O_8 by the nitric acid and the fission gases and NO_x, the reduced product of nitric acid, are released during the dissolution process. Virtually all available tritium becomes incorporated within the aqueous dissolver acid as HTO. The HOG from fuel shearing is led to a cyclone for particulate removal. The sheared fuel is then dissolved in nitric acid (Stream 6). The off-gases released during fuel dissolution are circulated to the dissolver off-gas treatment system (Stream 51). The dissolver off-gas is initially scrubbed for NO_x removal with oxygen being added (Stream 49) upstream of the NO_x scrubber slightly above the stoichiometric ratio needed to complete NO_x recombination to HNO_3.

It is assumed that approximately 1% of the irradiated fuel cesium and ruthenium inventory is released to the dissolver off-gas during fuel dissolution. However, these elements are prevented from entering the HOG system by the droplet separator, mist eliminator, and HEPA filter in the DOG system.

During NO_x scrubbing, approximately 50% of the iodine-129 released during fuel dissolution goes into solution in the nitric acid scrub liquid. This iodine is stripped from the nitric acid in an iodine stripper (Stream 53). The nitric acid leaving the iodine stripper, now free of I-129, is sent to the dissolvers and used for fuel dissolution (Stream 54), possibly after concentration adjustment. The iodine-rich stream leaving the stripper is fed back to the NO_x scrubber (Stream 55) where, based on the iodine partition coefficient, part of it goes to the gas phase (Stream 8, and is subsequently removed in the off-gas system by the iodine absorber) and the other part goes to the liquid phase (and is subsequently removed in the stream iodine stripper again - Stream 53). Hence, an iodine equilibrium is achieved.

The dissolver nitric acid containing the HTO is sent to the primary extraction unit, where the HTO remains in the high level liquid waste (HLLW). The HLLW is then evaporated to reduce the volume, and the condensate (containing the

---

*Nm^3/d, cubic meter per day at 0°C and 102 kPa.

HTO) is sent to a combined electrolysis/catalytic exchange unit from which the HTO is removed in a concentrated stream. The DOG is then sent to the HOG system (Stream 8), just downstream of the cyclone separator, and the combined off-gas (DOG and HOG) is passed through a droplet separator, a mist eliminator and a HEPA filter for mist removal, before it is pumped by the head-end blower to the tail end of the process for further treatment.

The following parameters and assumptions are used in the direct dissolution option/12,13/:

(a) Two dissolvers operating in tandem are assumed with each dissolver accepting two fuel charges of 1.25 Mg per day. The two units operate out-of-phase and are six hours apart at the starting points of their cycles. Dissolution is expected to take three hours, followed by digestion for another three hours to complete the cycle.

(b) It is assumed that 98.3% of krypton, 100% of carbon-14, 1.7% of tritium (as HT) and 94.6% of xenon are released to the dissolver off-gas during the dissolution process, as shown in Table 2.

(c) After fuel dissolution the dissolver is put under total reflux to drive out elemental iodine from the dissolver nitric acid. Ninety-three percent of the iodine is released to the dissolver off-gas during total reflux (Stream 51); however, about half of this goes into solution during NO_x scrubbing by HNO_3 and is subsequently stripped from the nitric acid in the iodine stripper (Stream 53). The iodine that remains in the gas phase after NO_x scrubbing goes to the head-end off-gas system (via Stream 8) and is caught in the iodine absorber.

(d) Approximately 1000 m^3/day (24.5 scfm) of air is added during fuel shearing (Stream 4). No additional purge air is added to the fuel dissolvers. Hence, the off-gas flow rate (DOG plus HOG) is approximately 1000 m^3/day.

The dissolver off-gas composition is shown in Table 2.

4.2 Voloxidation Process

The flow diagram and mass balances for the voloxidation option are shown in Figure 4. In this option, after the fuel is sheared, it is sent to a voloxidizer prior to being dissolved in nitric acid. In voloxidation, first developed at Oak Ridge National Laboratory/14/, UO_2 fuel is oxidized to U_3O_8 at 600°C in an air atmosphere, causing the fuel to expand, disintegrate into a fine powder, and separate from the fuel cladding. As a result, all available tritium is also oxidized and released from the irradiated fuel during voloxidation, and contamination of the dissolver nitric acid by tritiated water is prevented. A stoichiometric amount of oxygen is injected into the voloxidizer for the complete oxidation of UO_2. The tritium is evolved from the voloxidizer as HTO* vapour, with less than 0.1% as HT. The other fission gases (I-129, C-14, Kr-85, and Xe) are also released from the spent fuel during voloxidation, but only in varying fractional amounts.

---

* The tritium is also present as T_2O and DTO. However, HTO is the predominant form and this nomenclature is used in the text.

The head-end off-gas from fuel shearing and voloxidation is sent to a cyclone separator and a HEPA filter for particulate removal. The gas is then cooled to 40°C and sent to a molecular sieve drier (HTO trap) (Stream 2) where all the tritiated water vapour (HTO) in the off-gas is removed.

The voloxidized fuel is dissolved in nitric acid (as in the direct dissolution option), causing any gaseous radioisotopes remaining in the fuel (ie, I-129, C-14, Kr-85 and non-radioactive Xe) to be released. The operating mode of the dissolvers is identical to that described for the direct dissolution option. The DOG is then passed through an iodine stripper to steam strip the I-129 from the nitric acid vapour. Since the oxidation of U(IV) to U(VI) occurs in the voloxidizer and not in the dissolver, no NO_x are produced during fuel dissolution and therefore, a NO_x scrubber is not theoretically required. Even if a small amount of NO_x is produced during fuel dissolution, it would be recombined to form HNO_3 when the dissolver is in the digestion period under total reflux. Therefore, no NO_x leaves the dissolvers. The nitric acid from the iodine stripper, now free of I-129, is cooled and sent back to the dissolvers to be used for fuel dissolution (Stream 54).

The off-gas stream leaving the iodine stripper is passed through a droplet separator, a mist eliminator and a HEPA filter for removal of fine mist. The liquid collected in the droplet separator is recycled to one of the dissolvers on a daily basis. The DOG is then sent to the HOG system just downstream of the HTO molecular sieve drier (Steam 6) and upstream of the head-end blower before the combined stream is pumped to the tail end for further processing.

The quantity of off-gas in the voloxidation option (DOG plus HOG) is similar to that for the direct dissolution option. Therefore, the equipment sizes for both options are identical.

4.3 Off-Gas Tail End Process

From the head-end blower onwards, the off-gas system for the voloxidation option is similar to that of the direct dissolution option. The material balances, however, are slightly different since the distributions of the radionuclides as shown in Table 2 earlier are somewhat different between two processes.

The gas stream then enters the iodine absorbers for removal of I-129 (Stream 11). After iodine removal, the off-gas is sent to a catalytic oxygen recombiner (Stream 12) in which any remaining oxygen is reduced to water and any NO_2 (from the DOG) is reduced to N_2O and NO. The off-gas is then humidified and cooled to 30°C, to optimize CO_2 removal, and passed through a carbon dioxide absorber for removal of carbon-14 in the form of CO_2 (Stream 15). The residual moisture is then removed from the off-gas by a molecular sieve drier (Stream 17).

At this point, the off-gas consists mainly of nitrogen (from the carrier gas) and the noble gases xenon and krypton (Stream 19). This gas is then passed through the fluorocarbon selective absorption unit which consists of two separate columns (Figure 3). The first column recovers the more soluble xenon and the N_2O (Stream 20) and the second column recovers the less soluble krypton and the NO (Stream 22). After the removal of the noble gases, the remaining gas is sampled and monitored, and if no radioisotopes are detected, it is vented to the stack (Stream 23). If any radioisotopes are detected, the off-gas can be recycled to the combined off-gas system just upstream of the head-end blower.

4.4 Combined Electrolysis/Catalytic Exchange

This step is required for the direct dissolution process only. If direct dissolution is employed, the major portion (>99%) of tritium released during fuel dissolution becomes incorporated in the dissolver nitric acid as HTO. The dissolver nitric acid is then sent, along with the dissolved fuel, to the primary solvent extraction. Following the initial solvent extraction, the major portion of the tritium is in the HLLW, at an estimated concentration of 0.5 mg/kg/4/. The HLLW from the primary separation is then evaporated to reduce the volume, and the condensate (containing the tritiated water) is sent to the CECE unit at an estimated flow rate of 10 m^3/day.

A schematic illustration of the CECE unit is given in Figure 5. It comprises essentially an electrolyzer for gaseous hydrogen production, a counter-current packed bed reactor for tritium exchange between hydrogen gas and water, and possibly a recombiner for reconversion of the hydrogen to reflux water. As the water trickles down the column, it becomes more and more enriched in tritium. The hydrogen gas, which is already depleted in tritium relative to the electrolyte from which it evolved, becomes more and more depleted in tritium when it flows from bottom to top. A small tritium enriched water fraction (100 L/day) is removed from the electrolyzer for immobilization and storage.

The enriched gas stream of H_2 plus HT may be recombined with the O_2 evolved in the electrolyzer to regenerate H_2O/HTO which can then be recycled to the exchange column.

Prior to entering the CECE unit, the bleed stream is treated to remove nitric acid (estimated to be 0.01 M/15/ and those organics and fission products (eg, compounds of Ru) that volatilized during the HLLW concentration stage. These substances must be removed from the CECE feed stream to prevent accumulation in the electrolyser and/or absorption in the exchange column, which would be detrimental to the CECE process/15/. The bleed stream is passed first through a filter (optional) and then through two downflow fixed bed adsorbers filled with granular activated carbon to remove organics and fission products, at a flow rate of about two bed volumes per hour. Then, the NO_3^- ions from nitric acid are removed by passing through a downflow fixed bed anion exchange column, at a flow rate of about ten bed volumes per hour. For final purification, a commercial mixed bed ion exchange column can be used.

When the carbon of the first bed is exhausted, it is disposed of. The loaded anion exchange resin contains nearly no radioisotopes and it is regenerated with a NaOH solution.

The CECE process was originally developed by AECL/16/ for enriching D_2O; it was applied to tritiated water later by the Centre d'Etude de l'Energie Nucleaire (CEN), Belgium where it is called the ELEX process/17,18,19/. Here, a 0.12 m^3 H_2O (HTO) per day pilot detritiation unit, consisting of an 80 kW electrolyser and a 10 cm diameter tritium exchange column, has been constructed. The pretreatment process is relatively recent and has, therefore, only been tested in the laboratory scale to date.

It has been calculated that the ELEX process requires only five overall exchange transfer units to concentrate 90% of the original tritium in 1% of the original feed liquid volume, assuming a tritium-hydrogen separation factor of 10 for the water electrolysis and an exchange temperature of 50°C. Based on these

assumptions, the CEN has shown that the total operating costs for the ELEX process can be expected to be about two to four times lower than for water distillation and water electrolysis, two other possible methods for isotopic enrichment/17,18/. Also, very high enrichment factors (10^3 to 10^4) are possible with the ELEX process.

The disadvantages of the CECE unit are that severe containment restrictions would be required due to the potential for tritium diffusion and the high tritium activities (100 Ci/L) in the electrolytic cell. Also, the CECE unit has not yet been tested in a full-scale plant.

If the voloxidation option is employed, the CECE unit would not be required, since all available tritium would be concentrated in the HOG and would not become dispersed in the dissolver nitric acid.

5.0 WASTE CONDITIONING

If irradiated CANDU fuel were to be reprocessed, four volatile radioactive nuclides (tritium, iodine-129, carbon-14, and krypton-85) would be released from the fuel. They would have to be collected, conditioned, and encapsulated into a suitable form that would reduce the potential for migration or dispersion of the radionuclides by natural processes during storage, transportation, and disposal.

The conceptual design for the collection of the airborne radioactive nuclides was just discussed in the earlier sections. The conditioning, immobilization, and encapsulation are the subject for discussion in this section.

5.1 Tritiated Waste

The tritiated wastes from a fuel-reprocessing plant can be grouped into two categories, ie, tritium trapped in the matrix of the solid cladding hull, and tritium in aqueous solution.

The volume of cladding hull from PWR fuel was reported to be 15 m^3/GW(e)-a and 1400 tHM/a irradiated fuel could be generated from a 50 GW(e) power reactor/20,21/. This is equivalent to generating cladding hull at a rate of 0.54 m^3/tHM. The same rate is assumed for CANDU fuel throughout this study.

Tritium in the aqueous phase is either in tritiated water (HTO) or in tritiated nitric acid (TNO_3). In reprocessing, except through voloxidation, the tritiated species are distributed throughout the various streams in the process. As fresh water and nitric acid are added, the tritium solutions become progressively more diluted. On coastal sites, this large volume of diluted effluent can be discharged directly into the sea. In all other locations, this approach is prohibited. Concentrating it into a smaller volume of water is, therefore, highly desirable. Applying the approach developed in the Federal Republic of Germany/22/, the effluent volume can be reduced to 1000 - 1500 L/tHM for the conventional dissolution process by means of partial recycling of water and nitric acid and the segregation of tritium in the first aqueous head-end cycle. For the process with voloxidation the effluent volume can possibly be reduced to 2 - 20 L/tHM/21/. In the hypothetical reprocessing plant under present study, 2000 L/tHM and 20 L/tHM have been assumed for the processes with conventional dissolution and with voloxidation respectively.

Several solidifying media can be used for the immobilization of tritiated liquid waste. Materials such as inorganic hydrates, metal hydrides, organic polymers, or cement have been used to immobilize tritiated wastes. The cement form has been widely selected for tritiated waste since it is suitable for low level wastes as well as high level wastes and is also an acceptable medium for the fixation of wastes containing other radionuclides.

Immobilization of tritiated waste in cement was evaluated thoroughly by E.A. Mershad et al/23/. They found that an 81 kg 3 to 1 mixture of gypsum plaster to Portland cement can absorb 35 L of tritiated water and tolerate up to 70000 Ci in a 100 L primary container without excessive pressure during the initial decay. The tritiated water is fixed in a form of water of hydration of the salts making up the cement or in a form of water adsorbed in the gel formed by the compounds, as well as the water adsorbed as non-bonded water in the capillary void of the material. Some or all of the tritiated water in the cement can be released by evaporation and isotopic exchange with free water. Therefore, additional barriers around the cement are required to retain the tritium. Many suggestions, such as additives or coating material on the cement have been demonstrated with different degrees of success/21/.

Ontario Hydro Research Division has also been studying low level tritiated aqueous wastes for several years/24,25,26/. The tritiated water leach rate of water extendible polyester (WEP) medium was found to be four times lower than that of cement for 2 to 3 mCi tritiated water/25/. WEP also can be used for encapsulation; however, a high density polyethylene container has been shown to be a superior permeation barrier for tritium species/26/. Tritiated aqueous waste solidified in WEP and encapsulated in a 0.14 cm thickness polyethylene bottle would reduce the release rate to less than 1×10^{-3}% per day, an acceptable limit of release.

In the present study, cement and gypsum plaster mixture was considered a convenient and proven medium for low and high concentration tritiated wastes. WEP is a potential substitute for cement if it can be proven suitable for highly concentrated tritiated wastes. Encapsulation in a multiple barrier container is required to ensure at least 85 years storage (7 times half-life). A 100 L polyethylene drum could be employed as the primary container, which is then placed into a 115 L asphalt-lined steel drum for dry storage.

The following bases are recommended for the cost assessment:

	With Conventional Direct Dissolution	With Voloxidation
Tritiated water (L/tHM)	2000	20
Cement (kg/tHM)	1157	12
Gypsum plaster (kg/tHM)	3471	35

For a 5 tHM/d plant and assuming 35 L of tritiated water per 100 L drum, a total of 85 700 drums annually would be generated from the process with direct dissolution and 857 drums if voloxidation were used. To avoid this large quantity of drums, an alternative is to reduce the volume of the tritiated water before incorporating it with the cement mixture. As discussed earlier, the Elex/19/ or CECE (Combined Electrolysis and Catalytic Exchange) process can be used for concentrating the tritiated water. Volume reduction by a factor of 100 can conveniently be achieved, but apart from the capital investment, the key

operating cost would be the large amount of electricity required for the electrolysis.

For disposal, this cladding hull could be compacted to 80% of the metal density and fixed in cement in 200 L asphalt-lined drums prior to sealing with an asphalt cap. These sealed drums would be suitable for dry storage. For a 1500 tHM/a plant, 5400 drums would be required annually.

5.2 Iodine

Iodine-129, which is produced by nuclear fission and will be released during fuel reprocessing, has a half-life of 16 million years and has high mobility in the environment. It must be collected for storage or disposal. The collection method for iodine-129, using solid bed, silver nitrate impregnated silica gel or silver nitrate impregnated activated alumina, was discussed in Section 2. The iodine collection rate for a 1500 tHM/a reprocessing plant is estimated at 0.6 kg-atom/a which would require about 72 kg/a of silver at 90% utilization. Silver nitrate impregnated activated alumina or silica, loaded with 10 to 15% silver, would be employed.

Burger et al/27/ summarized the following criteria for choosing a form for fixation of iodine-129: solubility, thermal stability, cost and availability, toxicity, thermodynamic resistance to oxidation and hydrolysis, leaching of that compound in Portland type III cement, capture technology, disposal criteria or guidelines, and disposal site/strategy. Based on this checklist, Burger et al, recommended three choices: silver iodide in cement, barium, calcium, strontium, or mercuric iodide in cement, and iodine sodalite. Iodine sodalite was recognized to have great potential but has not yet been completely proven. As silver nitrate impregnated silica gel or silver nitrate impregnated activated alumina was recommended for the collection of iodine-129, silver iodide adsorbed on these materials and solidified in cement was chosen as the preferred form for disposal in this study. Recovery of silver is not recommended because the leaching resistance of the final product, eg, lead iodide, has not been established/28/.

Assuming $AgNO_3$ impregnated activated silica is employed, it would require 720 kg/a or 1.030 m^3/a of activated silica beds with a bulk density of 0.7 kg/L and with 0.1 silver mass fraction. The total waste volume would be 1 m^3/a approximate. After encapsulation in cement, the total volume would be 3 m^3/a.

The limits for iodine-129 discharge from a fuel cycle plant are 5 mCi/GW (e)-a, (40 CFR 190,1985). The environmental limits for adults are 2×10^{-9} Ci/m^3 in air and 1×10^{-5} Ci/m^3 in water and the environmental limits for minors are 2×20^{-11} Ci/m^3 in air and 6×10^{-8} Ci/m^3 in drinking water (10 CFR 20,1985). These absolute limits should not be exceeded and the disposal strategy should be based on these limits. Three ways for disposal of iodine-129 have been suggested: isotopic dilution by atmospheric dispersion, ocean disposal, and isolation in a geological repository for thousands of years. The first two methods are obviously undesirable. The Canadian concept of nuclear waste disposal in a deep vault in plutonic rock, is a form of geological repository that is relatively a better approach for the solution.

The effect of the iodine-129 release are doses to the local, regional and global population. In accordance with the study of Wushke, et al/29/, local doses would be much higher than regional or global doses during atmospheric discharge

through isotopic dispersion but, later, when most of the iodine-129 enters global circulation, the local, regional and global doses would become similar in magnitude. For ocean dumping, members of local and regional groups would receive local, regional and global doses; residents living in the Canadian Shield would receive doses only in global circulation. In accordance with the same study/29/, the collective dose from disposal in plutonic rock would be zero until about 20 000 years, when iodine diffuses through the rock and begins its discharge. Since it is estimated that nearly 99% of the iodine would decay before completing the discharge to the biosphere, the accumulated collective doses at 10^8 years is about two orders of magnitude lower than those in the other options. Nevertheless, for all three options, none would release doses higher than than the CFR's guideline limit with only one exception, ie, the local dose resulting from atmospheric dispersion.

The best choice, however, is isolation in a geological repository. It offers not only relatively lower collective doses but also an opportunity for monitoring the leakage path with certainty. The same cannot be achieved with the other options. The iodine-129 loaded bed solidified in cement cast in steel drums can be held in dry storage until the proposed deep vault in plutonic rock is built. Because the proposed deep vault is not yet committed, dry storage in a retrievable form will be required. This dry storage should be designed to last at least 50 years.

5.3 Carbon-14

Calcium carbonate produced from the gas-solid reaction is a stable chemical compound, but it must be isolated from the biosphere for a period of approximately 35 000 years (about 7 times the C-14 half-life). This isolation is required to prevent the reaction of calcium carbonate with CO_2 to form soluble $Ca(HCO_3)_2$ and the exchange of isotopes with carbon-bearing compounds with which it comes in contact particularly with carbon-12 compounds. This operation would require removal of the used $Ca(OH)_2$ beds, in a canister, from the removal system. As an alternative, a preliminary study was carried out by the Chemical Research Department to immobilize the beds inside the canister with a polymer such as epoxy. This could not be achieved successfully without considerable disturbance of the beds and supporting screens and this approach was discarded. The strategy adopted was to encapsulate the sealed canister with a concrete matrix and a carbon steel outer container to act as a mould and to provide protection to the waste form during transport and storage/30/. The other alternative is to extract the carbon-14 for commercial use if it is warranted by the market.

The quantity of carbon-14 dioxide generated from fuel reprocessing is very small (<0.2 kg $CaCO_3$/a). A 4 kg $Ca(OH)_2$ bed could last longer than two years even with an assumption to allow for substantial inleakages of carbon-12 dioxide. The used bed including steel canister could fit into a single steel drum for storage.

5.4 Krypton

Immobilization of trapped krypton can be accomplished in a metallic matrix or on zeolites. The metallic matrix has a capacity of 170 L (STP) of gas per litre of metal using copper, iron, aluminum or Monel/31/. Tingey at the Pacific Northwest Laboratory/32/ also reported on the implantation of krypton ions during the sputter deposition of metal such as iron, aluminum and nickel. The

release rate of the krypton that was trapped by sputter deposition of a metallic matrix is less than 2% in 10 years at 300°C. A slightly lower rate of only 1.8% in 10 years at 420°C was also claimed for krypton trapped in porous silica samples which were sintered at 900°C and 35 MPa.

Immobilization of krypton on 5A zeolites was described also by Penzhon et al from Karlsruhe/33/. Zeolites were loaded to about 22 cm^3/g(STP) at 300 bar pressure. No significant release was apparent at a temperature of 400°C while resistance to leaching in liquid water and to gamma irradiation was excellent. The fixation process in zeolites consists of two steps: gas densification and chemifixation. Densification can be achieved by sorption/desorption either at 4.7 bar and room temperature or at 1 bar at -20°C inside an autoclave. Under these conditions, enough gas will be adsorbed by the zeolite. Chemifixation takes place under a pressure of approximately 300 bar when the temperature is raised up to 520°C in the autoclave due to desorption and 22 cm^3/g (STP) krypton will be immobilized. Chemifixation is an irreversible process which takes place after the pores to the cavities are closed by a hydrothermal reaction. Loading or densification occurs by sorption which requires no high pressure. The autoclave is used only once and serves as a safe secondary containment during final disposal because of its inherent resistance towards internal or external corrosion, mechanical destruction and temperature excursions. Christensen et al/34/ reported similar findings on krypton trapped in zeolites, with capacities up to 70 cm^3/g (STP) and provided a cost estimate. They concluded that the process is economically feasible. No major technology development is required and the maximum krypton-85 release from a worst-case accident would result in maximum doses at the site boundary which are well below the release limit. Trapping krypton in zeolites is recommended in the present study.

The following parameters are recommended for scaling up equipment and making a cost estimate:

Bulk density, zeolite 5A	1.0 g/cm^3
Void fraction	40%

Fixation conditions 700°C and 100 MPa

Krypton produced per annum for 1500 tHM/a plant at 4.5 g mol/d	30 000 L/a (STP)
Chemifixation capacity	50 cm^3/g (STP)
Zeolite 5A required	605 kg/a
Total waste volume	1 m^3/a

The overall waste conditioning can be summarized in Table 3.

6.0 CONCLUSIONS

6.1 The technology for collecting individual radionuclides is available and can be chosen to match the preset selection criteria: simple, reliable, effective, safe, and economic.

6.2 A drying process based on molecular sieve is a good technique for trapping tritiated moisture.

6.3 Absorption of iodine on silver-doped solid sorbent specifically silver nitrate on alumina or silver nitrate on silica is a good choice due to their high efficiency and freedom from poisoning from NO_x and H_2O. The high stability with respect to heat and insolubility in water render these solid sorbents suitable for direct disposal.

6.4 The $Ca(OH)_2$ solid bed is selected for absorption of carbon-14 dioxide as its product $CaCO_3$ is a suitable form for further conditioning.

6.5 The selective absorption of noble gases in fluorohydrocarbon at low temperature and pressures is the choice for trapping krypton-85 and xenon as it provides a high purity product and maintains a low krypton inventory.

6.6 The processes selected above have been integrated successfully on paper to maintain the system pressure low to minimize the release of radioactive nuclides. Since the process is not yet proven it must be tested in the laboratory before it is scaled up for commercial applications.

6.7 Both front-end dissolution processes, direct dissolution and voloxidation, seem effective. The choice will depend on economics. In accordance with the recent analysis of N. Valliere/35/ the capital cost for the direct dissolution process is far greater than that of the voloxidation process. The obvious choice would be in favour of voloxidation.

6.8 Immobilization of separated tritium in cement and gypsum mixture is recommended. The cement paste can be cast in a 100 L polyethylene drum, the primary container, then placed into a 215 L asphalt-lined steel drum for dry storage. Prior to the waste conditioning, a volume reduction through FLEX or CECE process is highly desirable and recommended.

6.9 Silver iodide in cement is the preferred form for storage or disposal of the iodine-129. Recovery of silver is not recommended, because the leaching resistance for the final product, eg, lead iodide, has not been established.

6.10 The sealed canister of the carbon-14 collected in $CaCO_3$ form can be encapsulated in a concrete matrix and a carbon steel outer container to act as a mould and to provide protection to the waste form during transport and storage. The alternative would be to extract the carbon-14 for commercial use, if it is warranted by the market. The choice between the two alternatives depends upon economic merit.

6.11 It is recommended that krypton be immobilized and encapsulated through the chemifixation process into zeolite 5A. The autoclave employed for the fixation serves as the secondary containment for storage in an underground vault.

Approved by:

M.R. Booth
Acting Manager
Chemical Research Dept

Submitted by:

S.-D. Chang
Engineer, Process Development
Process Chemistry Section

Reviewed by:

S.H. Hawthorne
Unit Head, Process Development
Process Chemistry Section

SDC:kw

7.0 REFERENCES

1. H. Denber and J.G. Wilhelm, "Retention of Elemental Radioiodine by Deep Bed Carbon Filters Under Accident Conditions", Proceedings 17th DOE Air Cleaning Conference, Denver, Colorado, August, 1982, pp 248-76.

2. Darlington GS-A Design Requirements Emergency Filtered Air Discharge System, SCI 73750, Rev. 0, January, 1980.

3. S. Hattori et al, "Removal of Iodine from Off-Gas of Nuclear Fuel Reprocessing Plants with Silver-Impregnated Adsorbents", Proceedings of 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, August, 1984, pp 1343-60.

4. A.W. Jackson, "Evaluation of Radioactive Off-gas Treatment Technology", AECL Report TR-138 August, 1982.

5. G.L. Haag, "Carbon-14 Immobilization via the CO_2-$Ba(OH)_2$ Hydrate Gas-Solid Reaction", Proceedings of the 16th DOE Conference on Nuclear Air Cleaning Conference, San Diego, October, 1980.

6. C.H. Cheh and R.W. Glass, "$14CO_2$ Removal from Moderator Cover Gas", Ontario Hydro Report 82-342-H, October, 1982.

7. C.H. Cheh, R.W. Glass, and V.S. Chew, "Removal of Carbon-14 from Gaseous Streams", paper presented to the IAEA Seminar on the Testing and Operating of Off-Gas Cleaning Systems at Nuclear Facilities, Karlsruhe, Federal Republic of Germany, May 3-7, 1982.

8. J.A. Stone and D.R. Johnson, "Measurement of Radioactive Gaseous Effluent from Voloxidation and Dissolution of Spent Nuclear Fuel", Proceedings of the 15th DOE Nuclear Air Cleaning Conference, 1978, pp 570-83.

9. E. Henrich, et al, "Selective Absorption of Noble Gases in Freon-12 at Low Temperature and Atmospheric Pressure", Proceedings of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, August 1984, pp 959-81.

10. E. Henrich and R. Hufner, "I-129, Kr-85, C-14 and NO_x Removal from Spent Fuel Dissolver Off-Gas at Atmospheric Pressure and at Reduced Off-Gas Flow", Proceedings of the 16th DOE Nuclear Air Cleaning Conference, San Diego, October, 1980, pp 597-611.

11. E. Henrich, and R. Hufner, "Modular Design of a Reprocessing Plant Dissolver Off-Gas System", IAEA-CN-43-447, pp 455-73.

12. D.G. Boase, letter to S.J. Naqvi, March 20, 1985.

13. D.G. Boase, letter to S.J. Naqvi and C. Cheh, July 8, 1985.

14. J.A. Stone and D.R. Johnson, "Measurement of Radioactive Gaseous Effluents from Voloxidation and Dissolution of Spent Nuclear Fuel", Proceedings of the 15th DOE Nuclear Air Cleaning Conference, 1978, pp 570-83.

15. L.H. Baetsle Telex to N. Valliere, December 12, 1985.

16. M. Hammerli, W.H. Stevens, J.P. Butler, "Combined Electrolysis Catalytic Exchange (CECE) Process for Hydrogen Isotope Separation", Separation of Hydrogen Isotope (HK Rae Ed), American Chemical Society Symposium, ser. 68 (1978) 110.

17. A. Bruggeman et al, "Development of the Elex Process for Tritium Separation at Reprocessing Plants", Proceedings of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, August 1984, pp 495-509.

18. A. Bruggeman et al, "The Elex Process for Tritium Separation from Aqueous Effluents", Proceedings of Tritium Technology in Fission, Fusion and Isotope Applications, ANS National Topical Meeting, Dayton, Ohio, 1980.

19. A. Bruggeman et al, "Separation of Tritium from Aqueous Effluents", Commission of the European Communities Nuclear Science and Technology Report EVR-9107, 1984.

20. W.J. Holtslander, et al, "Management of Tritium at Nuclear Facilities", IAEA Publication, Vienna, 1984.

21. W.J. Holtslander and V. Tsyplenkov, "management of Tritium at Nuclear Facilities", Proceedings IAEA Conference, Seattle, May 1983, p 191, Vol 2.

22. E. Henrich, H. Schmieder, K.H. Neeb, "The Concentration of Tritium in the Aqueous and Solid Waste of LWR Fuel Reprocessing", Proceedings Management of Gaseous Wastes from Nuclear Facilities, IAEA, Vienna (1980), p 177.

23. E.A. Mershad, W.W. Thomasson, and J. Banby, "Tritiated Liquid Waste Packaging", Monsanto Research Corporation Report MLM-2440, UC-70, 1977.

24. S.H. Hawthorne, "Conditioning of Tritiated Wastes, Part I - Tritiated Water Immobilization", Ontario Hydro Research Division Report 82-351-K, 1982.

25. S.H. Hawthorne, "Condition of Tritiated Wastes, Part II - Solidification and Encapsulation", Ontario Hydro Research Division Report 84-6-K, 1984.

26. J.P. Krasznai, "Tritiated Waste Conditioning, Part III - Performance of Containerized and Encapsulated Waste Forms", Ontario Hydro Research Division Report 85-279-K, 1985.

27. L.L. Burger, R.D. Scheele and R.D. Weimers, "Selection of a Form for Fixation of Iodine-129", Pacific Northwest Laboratory Report PNL-4045, Richland, Wisconsin, December, 1981.

28. G.L. Haag, "Carbon-14 Immobilization via the CO_2-$Ba(OH)_2$ Hydrate Gas-Solid Reaction", Proceedings of the 16th DOE Conference on Nuclear Air Cleaning, San Diego, October 1980, pp 1095-1120.

29. D.M. Wuschke, J.W. Barnard, P.A. O'Connor, and J.R. Johnson, "Prediction of Local, Regional and Global Radiation Doses from Iodine-129 for Four Different Disposal Methods and an All-Nuclear Future", p 372, Proceedings

of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, Maryland, 1984, pp 732-751.

30. A.S. Williamson, Ontario Hydro Research Division, private communication, 1986.

31. D.S. Whitmell, "Choice of Materials for the Immobilization of Krypton-85 in a Metallic Matrix by Combined Ion Implantation and Sputtering", Proceedings of the 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore, Maryland, (1984), pp 667-682.

32. G.L. Tingey, E.D. McClanahan, M.A. Bayme, and W.J. Gray, "Solid State Containment of Noble Gases in Sputter Deposited Metal and Low Density Glasses", p 279, Proceedings of the IAEA Symposium on Management of Gaseous Wastes from Nuclear Facilities, February, 1980, Vienna.

33. R.D. Penzhon, H. Leitzig, K. Gunther, P. Schuster, and H.E. Noppel, "The Long Term Storage of Radioactive Krypton by Fixation in Zeolite 5A+", p 358, Proceedings of the 17th DOE Nuclear Air Cleaning Conference, August 2-5, 1982, Denver, Colorado.

34. A.B. Christensen, J.A. del Debbio, D.A. Knecht, J.E. Tanner and S.C. Cossel, "Immobilization of Krypton-85 in Zeolite 5A", p 333, Proceedings 17th DOG Nuclear Air Cleaning Conference, August 2-5, 1982, Denver, Colorado.

35. N. Valliere, "Off-Gas System for a CANDU Fuel Reprocessing Plant Engineering and Cost Analysis", Ontario Hydro Design & Development Division Report 85-420, May, 1986.

8.0 ACKNOWLEDGEMENTS

This work was funded by the Nuclear Materials Management Department of Ontario Hydro. We also would like to thank D.G. Boase of AECL and C. Frost of the Nuclear Materials Management Department of Ontario Hydro for supplyiong some of the reference material and for helpful discussions and comments on the report.

TABLE 1

COMPARISON OF VOLOXIDATION AND DIRECT DISSOLUTION

ITEM	VOLOXIDATION	DIRECT DISSOLUTION
1. Oxidize UO_2 to U_3O_8	by O_2	by HNO_3
2. NO_x Recovery	N/A	O_2
3. H-3 Recovery	Direct from Gas Phase	Via Extraction from liquid stream
4. I-129 Recovery	Direct from Gas Phase	Two steps: dissolved in liquid and then stripped
5. Air Requirement Nm^3/tHM^*	196	196
6. Process O_2 Requirement Nm^3/tHM	47	47
7. Tritiated Water Volume L/tHM	20	2000
8. Tritiated Water Volume With Volume Reduction L/tHM	N/A	20

* tHM = tonne(Mg) of Heavy Metal

Nm^3 = Volume in m^3 at STP

N/A = not applicable

TABLE 2

DISTRIBUTION OF VOLATILE RADIOACTIVE NUCLIDES IN 5000 Kg FUEL

NUCLIDES	IN FUEL K mol	IN OFF GAS VIA VOLOXIDATION K mol	%	IN OFF GAS VIA DIRECT DISSOLUTION K mol	%
Ru	2.475E-2	2.364E-4	1.0	2.364E-4	1.0
Cs	2.117E-2	2.058E-4	1.0	2.058E-4	1.0
H-3	2.333E-5	2.333E-5	100	1.667E-7	0.7
I-129	2.155E-3	2.155E-3	100	2.003E-3	93.0
C-14	6.500E-6	6.500E-6	100	6.500E-6	100
Kr-85	4.577E-3	4.577E-3	100	4.499E-3	98.3
Xe	4.912E-2	4.912E-2	100	4.646E-2	94.6

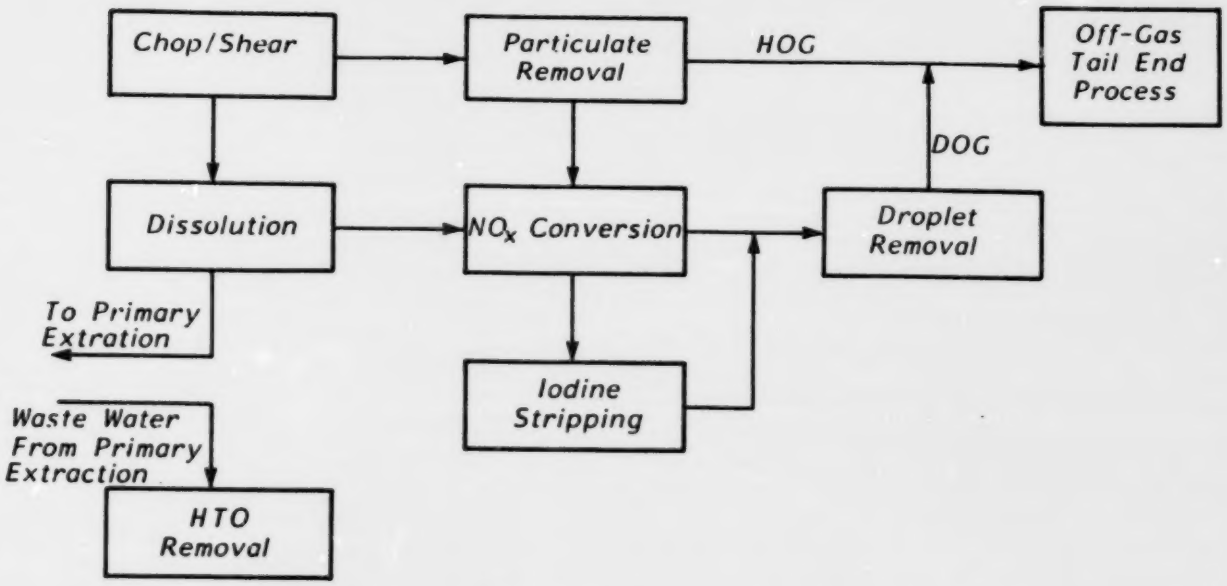
TABLE 3

SUMMARY OF WASTE CONDITIONING FOR STORAGE

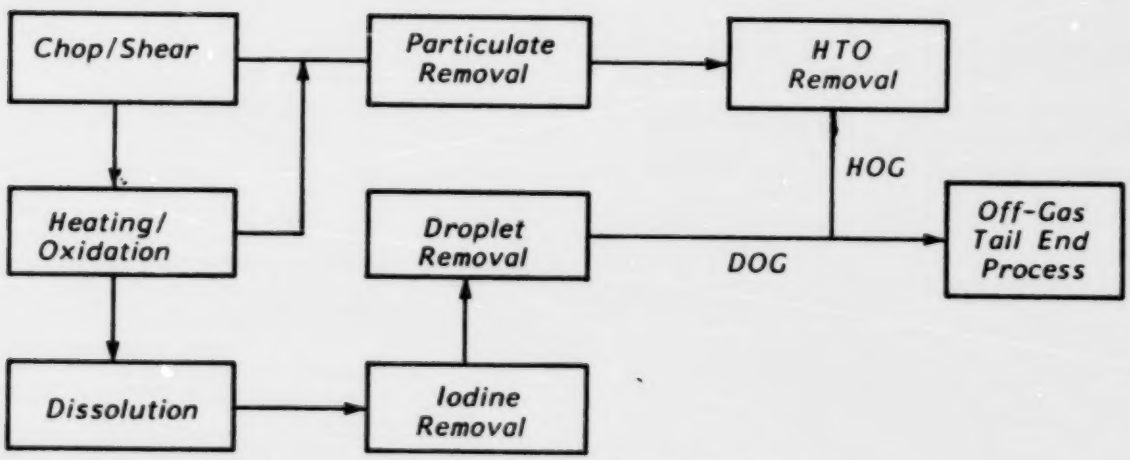
	Immobilization	Encapsulation	Additional Barrier	Waste Volume, m^3/a Preconditioned	Conditioned
H-3, Solid	Cement	Steel drum	Nil	810	1000
H-3, Liq	Cement and plaster mixture	Polyethylene drum	Asphalt coated mixture	30*	98
I-129	AgI in alumina or silica	Cement	Steel drum	1.0	3.0
C-14	$CaCO_3$ in canister	Concrete matrix	Steel drum	0.02	0.2
KR-85	Zeolites	Steel autoclave	Nil	30**	1.0

* Post volume reduction is assumed

** Gas at STP



(a), VIA DIRECT DISSOLUTION



(b), VIA VOLOXIDATION

FIGURE 1
OFF-GAS FRONT END PROCESSES

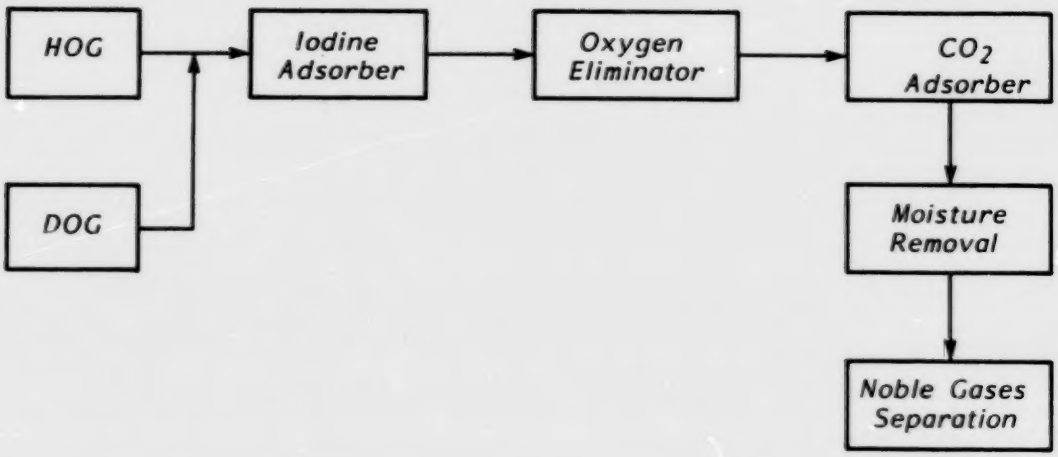
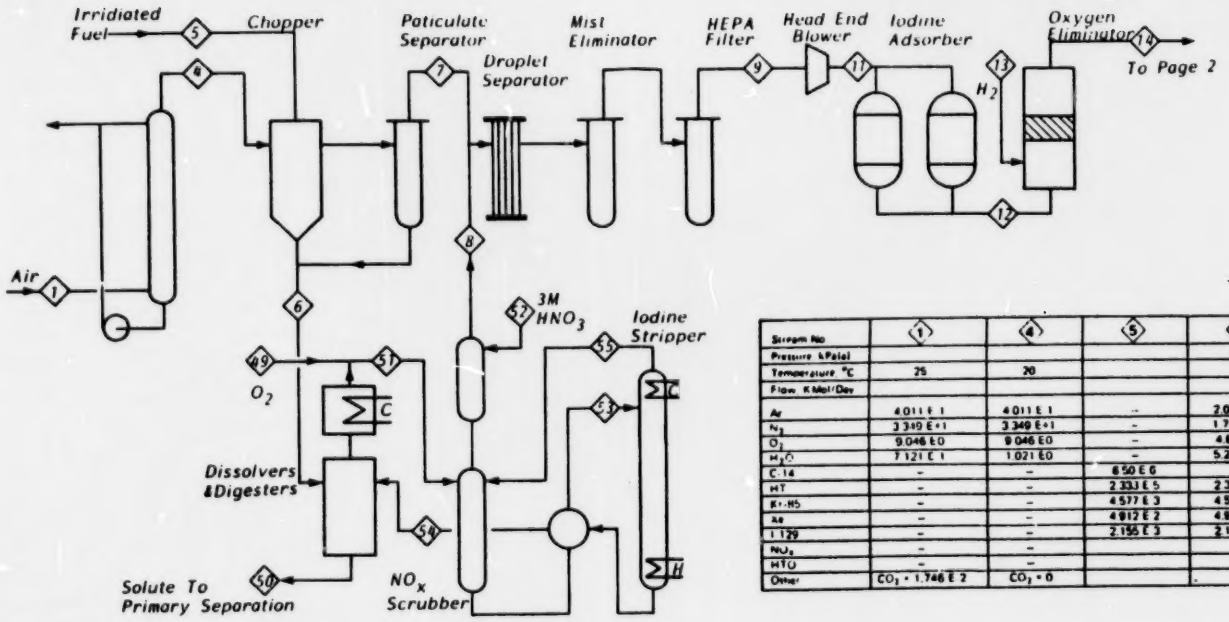


FIGURE 2
OFF-GAS TAIL END PROCESS

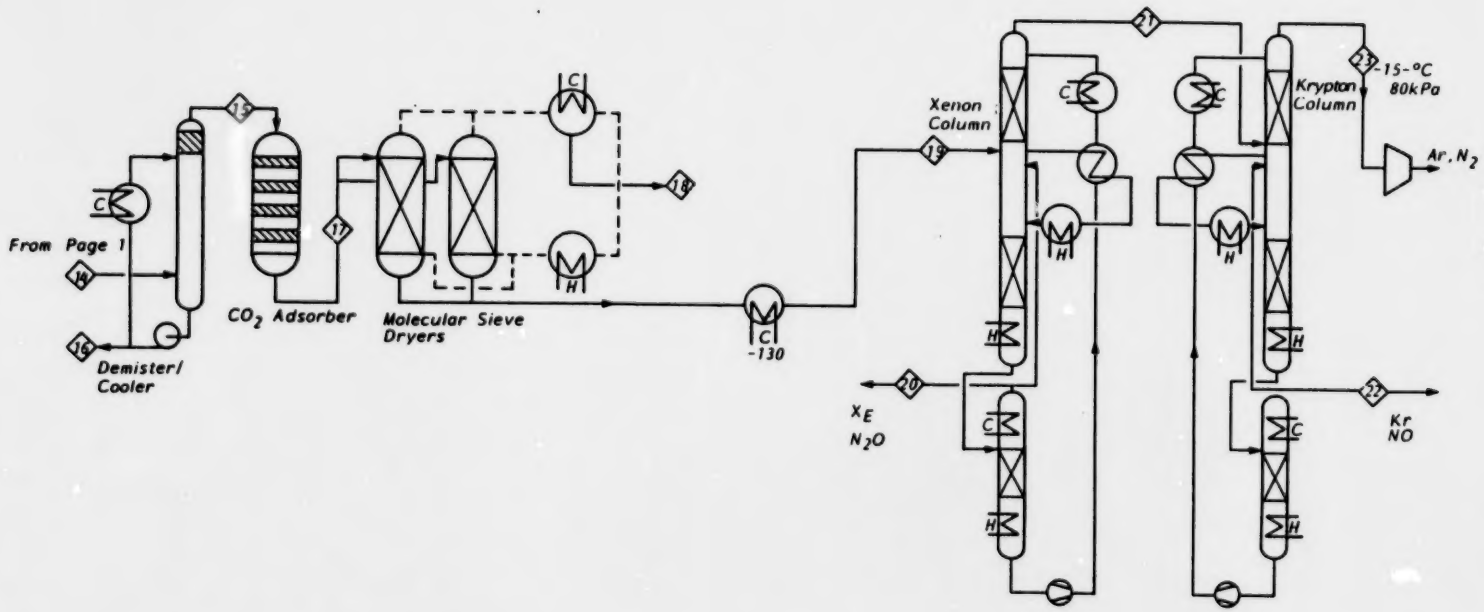


Stream No	1	4	5	6	7	8
Pressure, kPa(a)				95		90
Temperature, °C	25	20				20
Flow, Kilomol/Day						
Ar	4.011 E 1	4.011 E 1	-	2.051 E 1	1.900 E 1	2.051 E 1
N_2	3.349 E+1	3.349 E+1	-	1.712 E+1	1.637 E1	1.712 E1
O_2	9.046 E0	9.046 E0	-	4.625 E0	4.421 E0	4.625 E0
H_2O	7.121 E 1	1.021 E0	-	5.220 E 1	4.99 E 1	5.21 E 1
C-14	-	-	6.50 E 6	-	6.5 E 6	-
HT	-	-	2.333 E 5	2.316 E 5	1.867 E 7	-
Kr-85	-	-	4.577 E 3	4.577 E 3	-	4.499 E 3
Xe	-	-	4.912 E 2	4.917 E 2	-	4.646 E 2
I 129	-	-	2.155 E 3	2.155 E 3	-	2.003 E 3
NO_x	-	-			-	1.123 E 2
HTO	-	-			-	-
Other	CO_2 = 1.746 E 2	CO_2 = 0				HNO_3 = 8.18 E 2

Stream No	9	11	12	13	48	49	51	52	53	54	55
Pressure, kPa(a)	90	180	174								
Temperature, °C	40	44	44								
Flow, Kilomol/Day											
Ar	4.011 E 1	4.011 E 1	4.011 E 1			-	2.051 E 1				
N_2	3.349 E 1	3.349 E 1	3.349 E 1			-	1.712 E1				
O_2	9.046 E0	9.046 E0	9.046 E0		1.05 E1	-	1.512 E1				
H_2O	1.02 E0	1.02 E0	1.02 E0			7.084 E2	1.448 E0	7.077 E2	7.857 E2	7.071 E2	7.857 E1
C-14	6.50 E 6	6.50 E 6	6.50 E 6			-	-				
HT	1.867 E 7	1.867 E 7	1.867 E 7			2.316 E 5					
Kr-85	4.499 E 3	4.499 E 3	4.499 E 3			7.800 E 5	4.499 E 3				
Xe	4.646 E 2	4.646 E 2	4.646 E 2			2.88 E 3	4.646 E 2				
I 129	2.003 E 3	2.003 E 3	-			1.52 E 4	2.003 E 3		2.003 E 3		2.003 E 3
NO_x	1.123 E 2	1.123 E 2	1.123 E 2			-	2.10 E 1				
HTO						-	-				
Other				H_2 = 1.809 E1		HNO_3 = 6.18 E+1	HNO_3 = 3.03 E 3	HNO_3 = 4.2 E1	HNO_3 = 6.33 E1	HNO_3 = 6.29 E1	HNO_3 = 4.0 E1

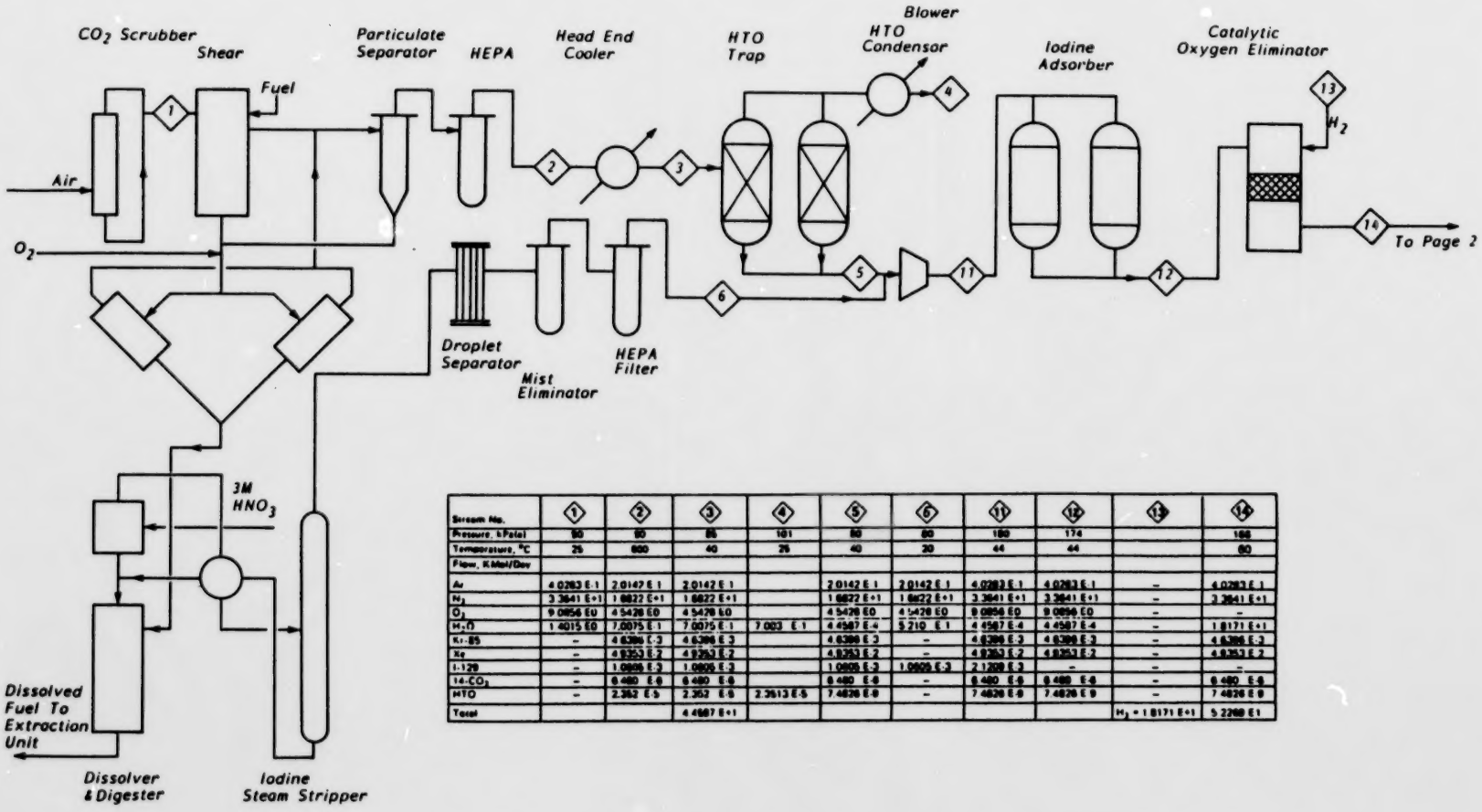
FIGURE 3

MATERIAL BALANCE FOR OFF-GAS SYSTEM WITH DIRECT DISSOLUTION (PAGE 1/2)



Stream No.	14	15	16	17	18	19	20	21	22	23
Pressure, kPa(a)	100	150	150	157	150	150	150	120	100	80
Temperature, °C	80	30	30	30		-130	-30	-120	-35	-150
Flow, Kmol/Day										
Ar	4.011 E-1	4.011 E-1		4.011 E-1		4.011 E-1	-	4.011 E-1		4.011 E-1
N_2	3.349 E1	3.349 E1		3.349 E1		3.349 E1	-	3.349 E1		3.349 E1
O_2	-	-		-		-	-			
H_2O	1.911 E1	1.45 E0	1.766 E1	1.450 E0	1.45 E0	3.366 E-5	-			
C-14	6.50 E-6	6.50 E-6		-			-			
HT	-	-		-			-			
Kr-85	4.499 E-3	4.499 E-3		4.499 E-3		4.499 E-3	-	4.499 E-3	4.499 E-3	
Xe	4.646 E-2	4.646 E-2		4.646 E-2		4.646 E-2	4.646 E-2	-		
I-129	-	-		-		-	-	-		
NO_x	1.123 E-2	1.123 E-2		1.123 E-2		1.123 E-2	-			
HTO	1.887 E-7	1.795 E-8	1.541 E-7	1.795 E-8	1.795 E-8	2.902 E-13	-			
Other							N_2O - 5.815 E-3	N_2O - 5.815 E-3	NO - 5.815 E-3	

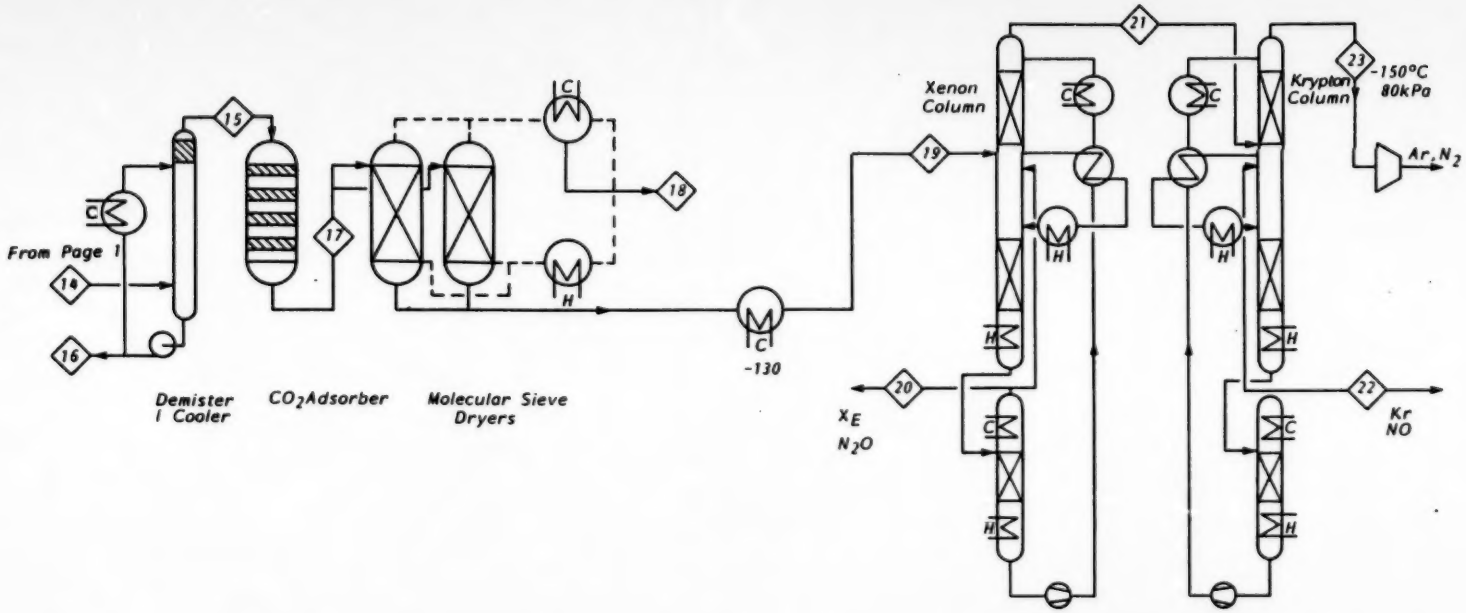
FIGURE 3
MATERIAL BALANCE FOR OFF-GAS SYSTEM
WITH DIRECT DISSOLUTION (PAGE 2/2)



Stream No.	1	2	3	4	5	6	11	12	13	14
Pressure, kPa(a)	90	90	85	101	80	80	180	174		168
Temperature, °C	25	800	40	25	40	30	44	44		60
Flow, K Mol/Day										
Ar	4.0283 E-1	2.0142 E-1	2.0142 E-1		2.0142 E-1	2.0142 E-1	4.0283 E-1	4.0283 E-1	–	4.0283 E-1
N_2	3.3841 E+1	1.6822 E+1	1.6822 E+1		1.6822 E+1	1.6822 E+1	3.3841 E+1	3.3841 E+1	–	3.3841 E+1
O_2	9.0856 E0	4.5428 E0	4.5428 E0		4.5428 E0	4.5428 E0	9.0856 E0	9.0856 E0	–	–
H_2O	1.4015 E0	7.0075 E-1	7.0075 E-1	7.003 E-1	4.4587 E-4	5.710 E-1	4.4587 E-4	4.4587 E-4	–	1.8171 E+1
Kr-85	–	4.6396 E-3	4.6396 E-3		4.6396 E-3	–	4.6396 E-3	4.6396 E-3	–	4.6396 E-3
Xe	–	4.8353 E-2	4.8353 E-2		4.8353 E-2	–	4.8353 E-2	4.8353 E-2	–	4.8353 E-2
I-129	–	1.0808 E-3	1.0808 E-3		1.0808 E-3	1.0808 E-3	2.1209 E-3	–	–	–
$^{14}CO_2$	–	6.480 E-6	6.480 E-6		6.480 E-6	–	6.480 E-6	6.480 E-6	–	6.480 E-6
HTO	–	2.362 E-5	2.362 E-5	2.3613 E-5	7.4826 E-9	–	7.4826 E-9	7.4826 E-9	–	7.4826 E-9
Total			4.4687 E+1						H_2 = 1.8171 E+1	5.2288 E1

FIGURE 4

MATERIAL BALANCE FOR OFF-GAS SYSTEM
WITH VOLOXIDATION (PAGE 1/2)



Stream No.	16	15	17	18	19	20	21	22	23
Pressure, kPa(a)	150	150	147	150	140	150	120	100	80
Temperature, °C	25	25	25		-130	-30	-120	-30	-150
Flow, K.Mol/Day									
Ar	–	4.0263 E-1	4.0263 E-1	–	4.0263 E-1		4.0263 E-1	–	4.0263 E-1
N_2	–	3.3641 E+1	3.3641 E+1	–	3.3641 E+1		3.3641 E+1	–	3.3641 E+1
O_2	–	–	–	–	–		–	–	
H_2O	1.7483 E1	6.8755 E-1	6.8775 E-1	6.8775 E-1	3.4787 E-5		–	–	
Kr-85	–	4.6396 E-3	4.6396 E-3	–	4.6396 E-3		4.6396 E-3	4.6396 E-3	
Xe	–	4.9353 E-2	4.9353 E-2	–	4.9353 E-2	4.9353 E-2	–	–	
I-129	–	–	–	–	–		–	–	
14-CO_2	–	6.480 E 6	–	–	–		–	–	
HTO	7.1883 E 9	2.833 E 10	2.833 E 10	2.8329 E-10	1.0 E 14		–	–	
Total			3.4787 E+1						

FIGURE 8

MATERIAL BALANCE FOR OFF-GAS SYSTEM
WITH VOLOXIDATION (PAGE 2/2)

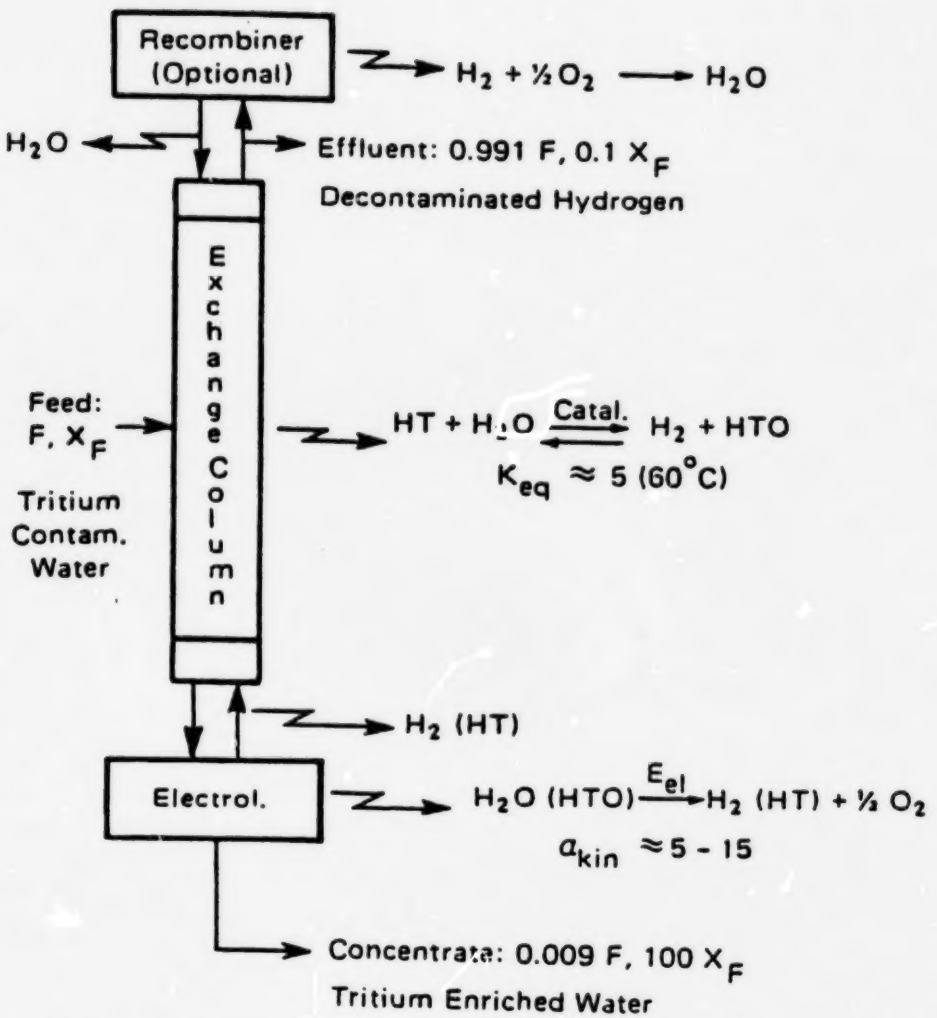


FIGURE 5
CECE PROCESS FOR DETRITIATION OF WATER

APPENDIX A

Process Development and Material Balances of the Direct Dissolution Process

1. Design Basis

1.1 Uranium in irradiated fuel, 5000 kg/d throughput, with five years cooling is assumed.

1.2 The direct dissolution process is assumed for the front end, two dissolvers are operating in tandem with each dissolver accepting two full charges of 1250 kg per day. The two units will operate out-of-phase by six hours apart in the starting point of their cycles.

1.3 Volatile species 98.3% of krypton, 93% of iodine, 100% of carbon-14, 0.7% of tritium, and 94.6% of xenon are released to the dissolver off-gas during the dissolution and digestion period. These fractions are obtained from back calculations of the inventory available and the data supplied by AECL.

1.4 One percent of the Cs and Ru inventory in the fuel is released but they are trapped in the HEPA filters; they would not enter into off-gas.

1.5 A carrying air at 978 Nm^3/d is used, half of which enters into the head end off-gas, the other half of which enters into the dissolver off-gas.

1.6 The carbon dioxide potentially generated from graphite lubricant adhering to fuel bundles is not taken into account.

1.7 Oxygen, in addition to air, in an amount of 235.2 Nm^3/d is added to the

NO_x scrubber, the theoretical amount required, to convert NO_x to nitric acid.

1.8 Inventory of radioactive nuclides contained in the irradiated fuel with 5000 kg/d uranium in fuel is distributed as follows:

Nuclides	Inventory kg/d	Inventory kmol/d	In DOG/HOG %	In DOG/HOG kmol/d	In HLLW kmol/d
K-85	0.389	4.577E-3	98.3	4.499E-3	7.800E-5
I-129	0.278	2.155E-3	93	2.003E-3	1.520E-4
C-14	9.1E-5	6.500E-6	100	6.500E-6	--
H-3	7.0E-5	2.333E-5	0.7	1.667E-7	2.316E-5
Xe	6.45	4.912E-2	94.6	4.646E-2	2.660E-3
Cs	2.9	2.117E-2	1.0	2.058E-4	2.096E-2
Ru	2.5	2.475E-2	1.0	2.364E-4	2.451E-2

Notes:

DOG - Dissolver off-gas
HOG - Head end off-gas
HLLW - High level liquid waste

2. Material Balances

2.1 Carrying Air

Air is employed to carry the airborne radioactive nuclides; before its use carbon dioxide content must be removed in order to avoid overloading the carbon dioxide adsorbent bed unnecessarily. The carbon dioxide removal can simply be done by scrubbing with recycling caustic solution in a scrubber.

About 500 Nm^3/d caustic treated air introduced into the chopping glove box goes with chopped fuel into a dissolver in action. An equal amount of air carries particulates into the particulate separator. The air stream comes out from the

separator and is joined by the air stream from the processes: dissolution and NO_x scrubbing. This combined air stream flows forward for further treatment.

Assume 978 Nm^3/d or 1256 kg/d (196 Nm^3/tU) air at 25C and 50% relative humidity, the humidity of this stream

Hs = 1.01 E-2 kg H_2O/kg dry air

The H_2O carried by the stream entering the CO_2 scrubber

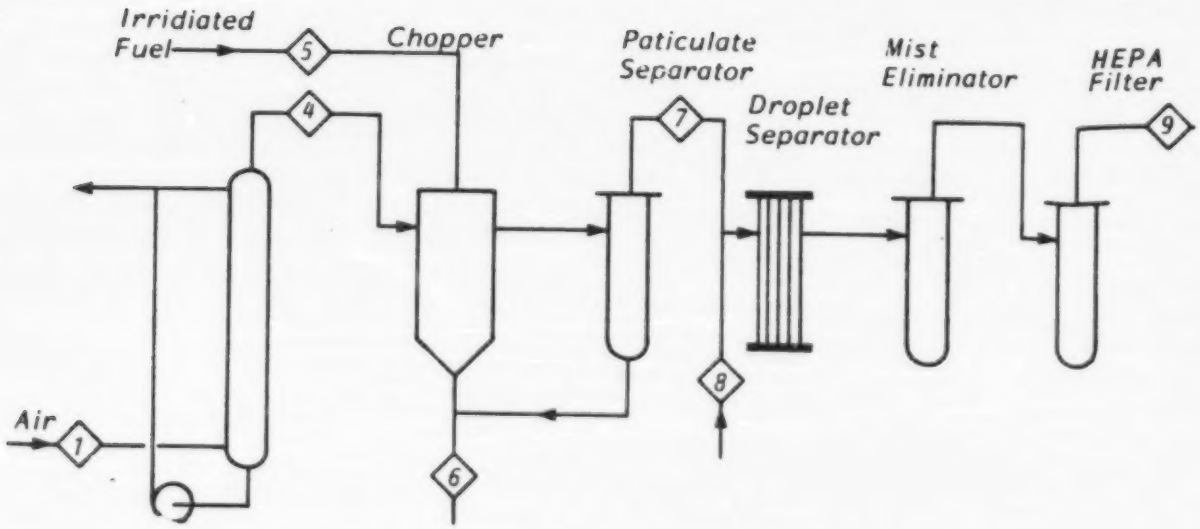
$$= \frac{(1256)\ (1.01E\text{-}2)}{(1\text{-}1.01E\text{-}2)} = 12.82 \text{ kg/d}$$

or 0.7121 kmol/d

Air in dry basis is assumed to be a mixture consisting of argon 0.934%, nitrogen 78% and oxygen 21.066%.

2.2 Chopping

Chopping of irradiated fuel takes place under an air blanket. The air will carry away airborne radioactive nuclides and carry fuel to dissolution. The amount of air 196 Nm^3/tU is considered sufficient to cover the chopping and as carrier gas in the voloxidation process. The same amount of air is considered sufficient for the direct dissolution process. It is interesting to note that this amount of air is about twice the optimum quantity, 100 Nm^3/tU, as suggested by Henrich and Hufner (Proceedings 16th DOE Nuclear Air Cleaning Conference, San Diego (1980), p 597).



Stream 4

The CO_2 scrubber is operated at 20°C; the air evolved from it is saturated with moisture. The air flow on dry basis is

= 43.66 - 0.7121 = 42.95 kmol/d

H_2O carried at 20°C

$= (42.95)(29)(1.475 \times 10^{-2}) = 18.37$ kg/d

or 1.021 kmol/d

From air compositions, and radionuclides in the irradiated fuel the following streams were calculated.

	1	4	5	6	7	8	9
Air components:							
Ar	4.011E-1	4.011E-1	-	2.051E-1	1.960E-1	2.015E-1	4.011E-1
N_2	3.349E1	3.349E1	-	1.712E1	1.637E1	1.712E1	3.349E1
O_2	9.046E0	9.046E0	-	4.625E0	4.421E0	4.625E0	9.046E0
H_2O	7.121E-1	1.021E0	-	5.220E-1	4.990E-1	5.210E-1	1.020E0
kmol/d	4.366E1	4.396E1		2.247E1	2.149E1		
kg/d	1256	1256		645	616.6		
Temp C	25	20		20	20		
Radionuclides							
Kr	-	-	4.577E-3	4.577E-3	-	4.499E-3	4.499E-3
Xe	-	-	4.912E-2	4.912E-2	-	4.646E-2	4.646E-2
I	-	-	2.155E-3	2.155E-3	-	2.003E-3	2.003E-3
C-14 O_2	-	-	6.500E-6	-	6.500E-6	-	6.500E-6
HT	-	-	2.333E-5	2.316E-5	1.667E-7	-	1.667E-7
Nonvolatile Components			Not listed	Not listed	trace	NO_x 1.123E-2	1.123E-2

Stream 8

Air flow = 21.947 kmol/d = 635.41 kg/d
H_2O carried by this stream at 20°C
= (635.41)(1.475 x 10^{-2}) = 9.372 kg/d
= 0.521 kmol/d

NO_x at 500 ppm
= (21.947 + 0.521) * 500/10^6 = 1.123 E-2

Stream 9 = 8 + 7

2.3 Particulate and Mist Elimination

A series of filters are employed to eliminate the airborne solid particulates, liquid droplets, and liquid mist. The head end off-gas, bearing particulates, droplets, and mist, first enters into a mechanical particulate separator where solid particulate is separated and returned to the dissolvers. The gas is then joined by the dissolver off-gas and enters into the coarse droplet separator and then the recleanable mist eliminator. The mist eliminator is so designed that high retention factors are attained for airborne droplets and

solid particulates. Thus, these prefilters extend the service life of the succeeding HEPA filters and iodine filters which are in series with the prefilters. This approach is similar to that recommended by Furrer et al. (Proceedings 16th DOE Nuclear Air Cleaning Conference, San Diego, October, 1980, pp 566-584.)

2.4 Dissolution and NO_x Scrubbing

When UO_2 dissolves in nitric acid solution the uranium is oxidized to $UO_2(NO_3)_2$; meantime, nitric acid is reduced to NO and NO_2.

$$2UO_2 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + NO + NO_2 + 3H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow HNO_3 + NO$$

(a) Without NO_x recovery and 5000 kg/d uranium or 21.0 kmol/d throughput the chemical requirements are:

$HNO_3/U = 3.0$, $HNO_3 = 3 \times 21.0$ or 63 kmol/d
$O_2/U = 0.5$, $O_2 = 0.5 \times 21$ or 10.5 kmol/d or 47 m^3/tu

and NO_x and H_2O are expected:

$H_2O/U = 1.5$ $H_2O = 1.5 \times 21 = 31.5$ kmol/d
$NO_x/U = 1.0$ $NO_x = 21$ kmol/d
NO_2/NO ratio = 1.0

(b) With NO_x recovery,

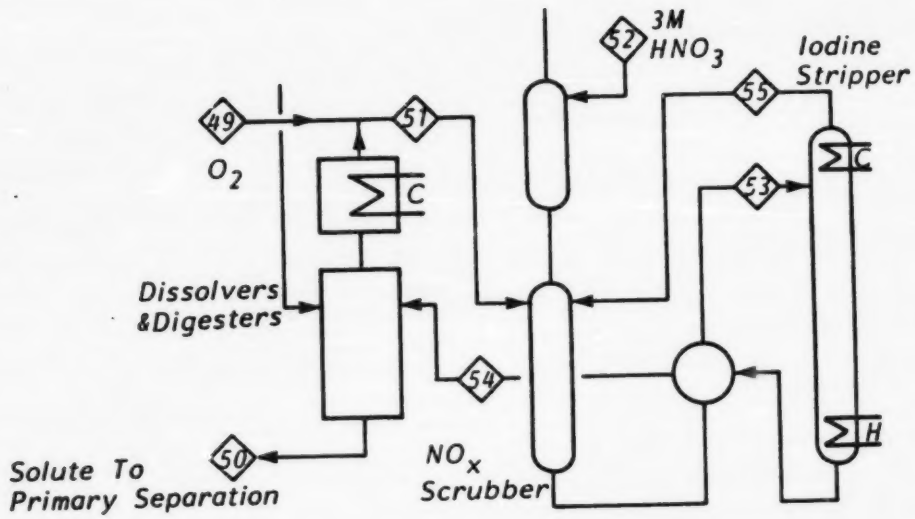
$HNO_3/U = 2.0$ $HNO_3 = 2 \times 21 = 42$ kmol/d
$O_2/U = 0.5$ $O_2 = 0.5 \times 21 = 10.5$ kmol/d
$H_2O/U = 1.0$ $H_2O = 21$ kmol/d
$NO_x/U = 0.0$ $NO_x = 0.0$

(c) By comparing with literature reported (Henrich and Hufner, Proceedings 16th DOE Nuclear Air Cleaning Conference, San Diego (1980), p 597), the results are tabulated as follows:

	This Work		
	Without NO_x Recovery	With NO_x Recovery	Henrich et al
HNO_3, 3M, m^3/tU	4.2	2.8	2
kmol/d	63	42	30
Process oxygen Nm^3/tU	47	47	45
Nm^3/d	235	235	225
NO_x, ppm	0	0	500 - 1000

It can be seen that the calculated nitric acid requirements are greater than that reported by Henrich et al and the process oxygen requirements are comparable. In this work fumeless dissolution is assumed or no NO_x is generated; this compares to 500 to 1000 ppm reported by Henrich et al.

The other streams as indicated in the following sketch are calculated as follows:



Stream 51 :

	kmol/d	MW	kg/d
$NO + NO_x$ =	21	38	798
O_2 =	10.5	32	321.3
Air at 100 Nm^3/tU	2232	29	647.3
			1776.6

+ radionuclides I, $C14O_2$, Kr, and Xe from Stream 6 less those from Stream 50 .

H_2O carried
$= (1766.6)(14.75 \times 10^{-3}) = 26.06$ kg/d
$= 1.448$ kmol/d

HNO_3 carried
$= (1.448)(1.49/735.6) = 0.003$ kmol/d

Stream 52 :

3M HNO_3, p = 1.097, HNO_3 = 17.2 wt%
kmol/d H_2O associated with 42 kmol/d HNO_3

$$\text{or } \frac{(42)(63)}{(42)(63) + (\chi)(18)} \times 100 = 17.2\%$$

Solve for χ

$\chi = 707.7$ kmol/d

Stream 50 = Streams 52 + 6 - 8

HTO
$HNO_3 = 42.0 + 0 - (8.18E\text{-}2 + 1.152E\text{-}2) = 41.9$ kmol/d
$H_2O = 707.7 + 7.74E\text{-}1 - 5.755E\text{-}1 = 706.4$ kmol/d

Stream 54 = Streams 50 + 51 - 6

$HNO_3 = 41.9 + (0.003 + 21) - 0 = 62.09$ kmol/d	3962.7 kg/d	
$H_2O = 706.4 + 1.448 - 7.24E\text{-}1 = 707.12$ kmol/d	12728 kg/d	
$HNO_3 + H_2O$ =	16691 kg/d	

HNO_3 wt% = 3962.7/16691 = 23.7 wt%
Sp.gr. of HNO_3 23.7wt% at 104.1°C = 1.0755
Partial pressure at 104.1°C
$P_{HNO_3} = 3.73$ mm Hg, $P_{H_2O} = 734.3$, $P_T = 737.2$

HNO_3 concentration

$$= \frac{62.9 \times 1000}{16691/1.0755} = 4.05 \text{ M}$$

Stream 55 :

Assume 1/10 fraction of water evaporated
9/10 fraction of water stayed down

H_2O in Stream 55 = H_2O in Stream 54 - 9
= 707.1/9 = 78.57 kmol/d

HNO_3 carried
= (78.57)(3.73)/(734.3)
= 0.4 kmol/d
and plus iodine in the stream

Stream 53 :

A component in Stream 53 = the same component in Stream 54 and in Stream 55

HNO_3 = 62.9 + 0.4 = 63.3 kmol/d
H_2O = 707.1 + 78.57 = 785.7 kmol/d
and plus iodine in the stream

The results may be summarized as follows:

Stream	50	51	52	53	54	55
Ar		2.051E-1				
N_2		1.712E1				
O_2		1.513E1				
H_2O	7.064E2	1.448E0	7.077E2	7.857E2	7.071E2	7.857E1
C-14						
HT	2.316E-5					
Kr-85	7.800E-5	4.499E-3				
Xe	2.660E-3	4.646E-2				
I-129	1.520E-4	2.003E-3				
NO_x	-	2.100E1				
HIO	-					
Other (HNO_3)	4.190E1	3.03E-3	4.2E1	6.33E1	6.29E1	40E1

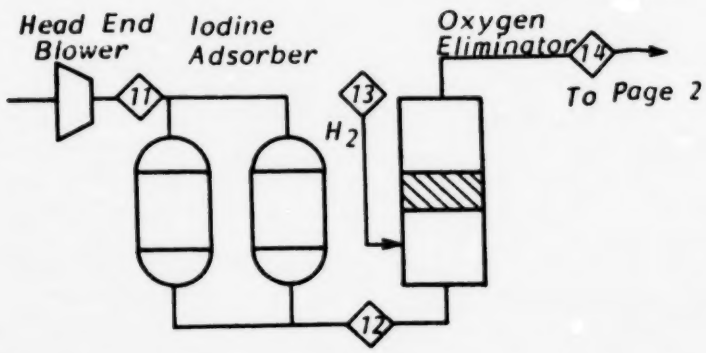
2.5 Off-Gas Clean-up Train

The dissolved off-gas evolved from the NO_x scrubber is joined by the head end gas up stream of the HEPA filter at which liquid droplets and mist are eliminated. Then, the combined gas is pumped by the head end compressor for further treatment.

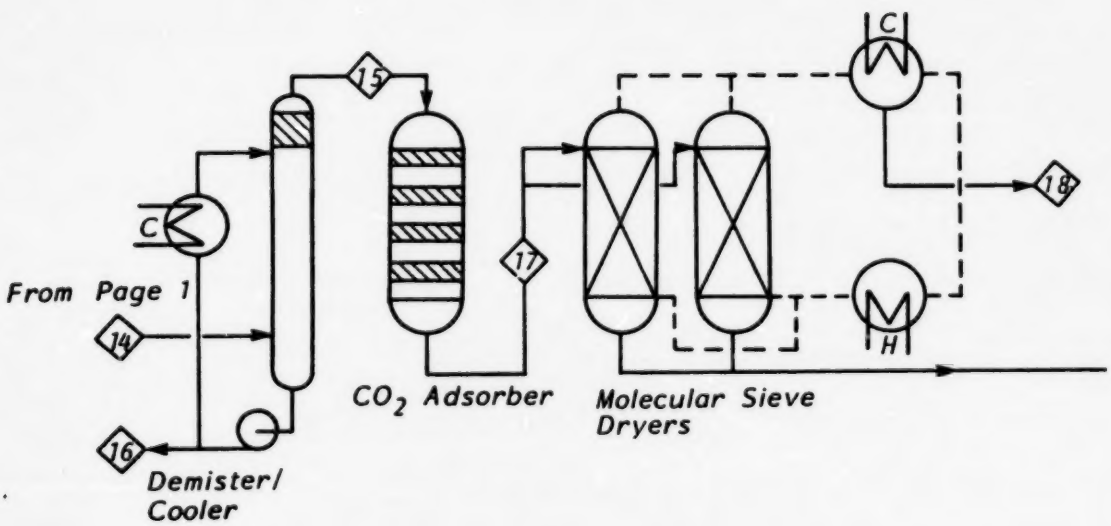
The first step in the treatment is to remove the iodine; the second step is to eliminate the oxygen; the third step is to remove the moisture before feeding into the noble gas separation unit.

The iodine adsorber is packed with silver alumina (AgA) or silver silica gel (AgS) beds: about 10 cm depth for each of the multiple layers. The loading capacity is expected to be 100 mg/g of adsorbent which consists of about 10% silver. The silver utilization is expected over 80%. The linear velocity can be designed at 5 cm/s in accordance with the experience reported by Hattori et al. (Proceedings 18th DOE Nuclear Airborne Waste Management and Air Cleaning Conference, Baltimore (1984) pp 1343-60.) The number of layers or the amount of silver alumina or silver silica gel is to be determined by the amount of iodine anticipated during the planned operating period.

The absorber beds could be used once through; they could also be used repeatedly through regeneration. The ultimate choice depends on the balance of the adsorbent cost and the regeneration cost. Silver alumina or silver silica gel is chosen because either one is highly resistant to poison from moisture and from NO_x. These poisonous gases are expected to be present in the stream.



Stream	9	11	12	13	14
Ar	4.011E-1	4.011E-1	4.011E-1		4.011E-1
N_2	3.349E1	3.349E1	3.349E1		3.349E1
O_2	9.046E0	9.046E0	9.046E0		-
H_2O	1.020E0	1.020E0	1.020E0		1.911E1
C-14	6.500E-6	6.500E-6	6.500E-6		6.500E-6
HT	1.667E-7	1.667E-7	1.667E-7		-
Kr-85	4.499E-3	4.499E-3	4.499E-3		4.499E-3
Xe	4.646E-2	4.646E-2	4.646E-2		4.646E-2
I-129	2.003E-3	2.003E-3	-		-
NO_x	1.123E-2	1.123E-2	1.123E-2		1.123E-2
HTO	-	-	-		1.667E-7
Other	-	-	-	H_2 1.809E1	-



Stream	14	15	16	17	18	19
Ar	4.011E-1	4.011E-1		4.011E-1		4.011E-1
N_2	3.349E1	3.349E1		3.349E1		3.349E1
O_2	-	-				
H_2O	1.911E1	1.450E0	1.766E1	1.450E0	1.450E1	3.395E-5
C-14	6.50E-6	6.50E-6		-		
HT	-	-		-		
Kr-85	4.499E-3	4.499E-3		4.499E-3		4.499E-3
Xe	4.646E-2	4.646E-2		4.646E-2		4.646E-2
I-129	-	-		-		
NO_x	1.123E-2	1.123E-2		1.123E-2		1.123E-2
HTO	1.667E-7	1.265E-8	1.541E-7	1.265E-8	1.265E-8	2.902E-13
Other	-	-				

Stream 15

Moisture carried at 30°C
= (955.7)(2.731 x 10^{-2}) / 18 = 1.450E0 kmol/d

Stream 19

1 ppm moisture carried:
HTO = (3.395E1)(10^{-6})(1.265E-8)/(1.450E0) = 2.402E-13
H_2O = (3.395E1)(10^{-6}) = 3.395E-5

2.6 Selective Absorption of Noble Gases

The selective absorption process for the removal of noble gases is preferred for the following reasons:

- the absorption is done at atmospheric pressure.

- under steady state Kr-85 inventory is considerably lower.

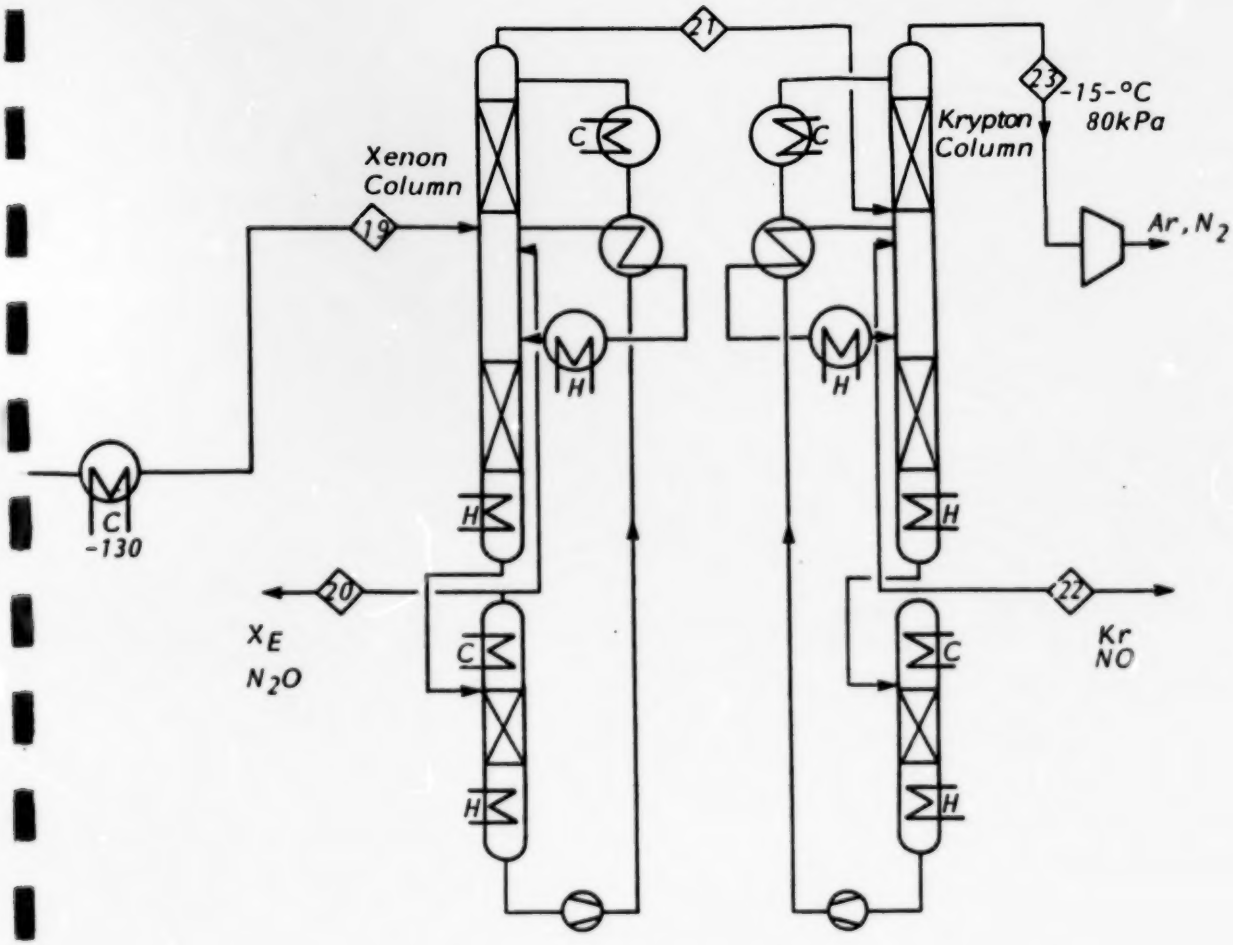
- the selective absorption in freon is insensitive to impurities thus reducing the pre-cleaning requirements and the sensitivity to malfunction of upstream equipment.

As described by Henrich and Hufner (16 DOG Nuclear Air Cleaning Conference, San Diego, 1980, pp 597-611) the next sketch shows the noble gas scrubber. The

defrostable input cooler reduces the DOG temperature to less than the lowest temperature in the subsequent scrubber, thus avoiding plugging by freezing of the components. The N_2O is the critical component, limiting the lowest operating temperature to about $-125^{o}C$. Keeping the amount of freezing prone gas components low in the system permits defrost cycles of several hundred hours. Any malfunction of upstream equipment can also be corrected by shortening cycle time, thus giving additional on-line redundancy.

Each of the following Kr and Xe scrubbers consists of three functional packed column sections: absorber, fractionator and stripper; the freon (R-12) flow is by gravity. The higher boiling components Xe, N_2O and $^{14}CO_2$ are selectively absorbed in the first Xe scrubber; co-absorbed Kr is removed from the liquid R-12, together with some O_2 and N_2 at a fractionator boil-up rate of about 3%. The absorbed gases Xe, N_2O and $^{14}CO_2$ are removed completely in the stripper at a boil-up rate of about 16%. The stripper is usually separated from the fractionator at the gas side, not at the liquid one. The stripped liquid R-12 is recycled to the absorber, via a heat exchanger for energy economy. A smaller heater and cooler corrects the incomplete heat exchange.

The same operations occur in the Kr scrubber at different flow ratios and boil-up rates and at still lower temperatures in the absorber. The R-12 concentration in the purified off-gas is below the maximum permissible concentration, therefore an additional R-12 removal system is avoided.



Stream	19	20	21	22	23
Ar	4.011E-1				4.011E-1
N_2	3.349E1				3.349E1
H_2O	3.395E-5				
Kr	4.499E-3		4.499E-3	4.499E-3	
Xe	4.646E-2	4.646E-2			
NO_x	1.123E-2	5.615E-3	5.615E-3		5.615E-3
HTO	2.902E-13				

APPENDIX B

Process Development and Material Balances of the Voloxidation Process

1. Design Basis

1.1 Uranium in irradiated fuel, 5000 kg/d throughput, with five years cooling is assumed.

1.2 The voloxidation is assumed for the front end process. This process involves oxidizing the sheared fuel in air up to 600°C thus causing the fuel to expand, disintegrate into a fine powder and separate from the cladding.

1.3 All volatile species, ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I are released during the oxidation of UO_2 to UO_3.

1.4 One percent of the Cs and Ru inventory in the irradiated fuel is released but they are trapped in the HEPA filters; they would not enter into off-gas.

1.5 A carrying air at 978 Nm^3/d at 20°C and 50% relative humidity is employed after removal of CO_2 at 25°C.

1.6 The carbon dioxide potentially generated from graphite lubricant adhering to fuel bundles is not taken into account.

1.7 Oxygen, in addition to air, in an amount of 235.2 Nm^3/d is introduced to the voloxidizers to help oxidizing UO_2 to UO_3.

1.8 Inventory of radioactive nuclides contained in the irradiated fuel with 5000 kg/d uranium in fuel is distributed as follows:

Nuclides	Inventory kg/d	Inventory kmol/d	In DOG/HOG %	In DOG/HOG kmol/d
Kr-85	0.389	4.577E-3	100	4.577E-3
I-129	0.278	2.155E-3	100	2.155E-3
C-14	9.1E-5	6.500E-6	100	6.500E-6
H-3	7.5E-5	2.333E-5	100	2.333E-5
Xe	6.45	4.912E-2	100	4.912E-2
Cs	2.5	2.117E-2	1.0	2.058E-4
Ru	2.9	2.475E-2	1.0	2.364E-4

Notes:

DOG - Dissolver off-gas
HOG - Head end off-gas

2. Material Balances

2.1 Carrying Air

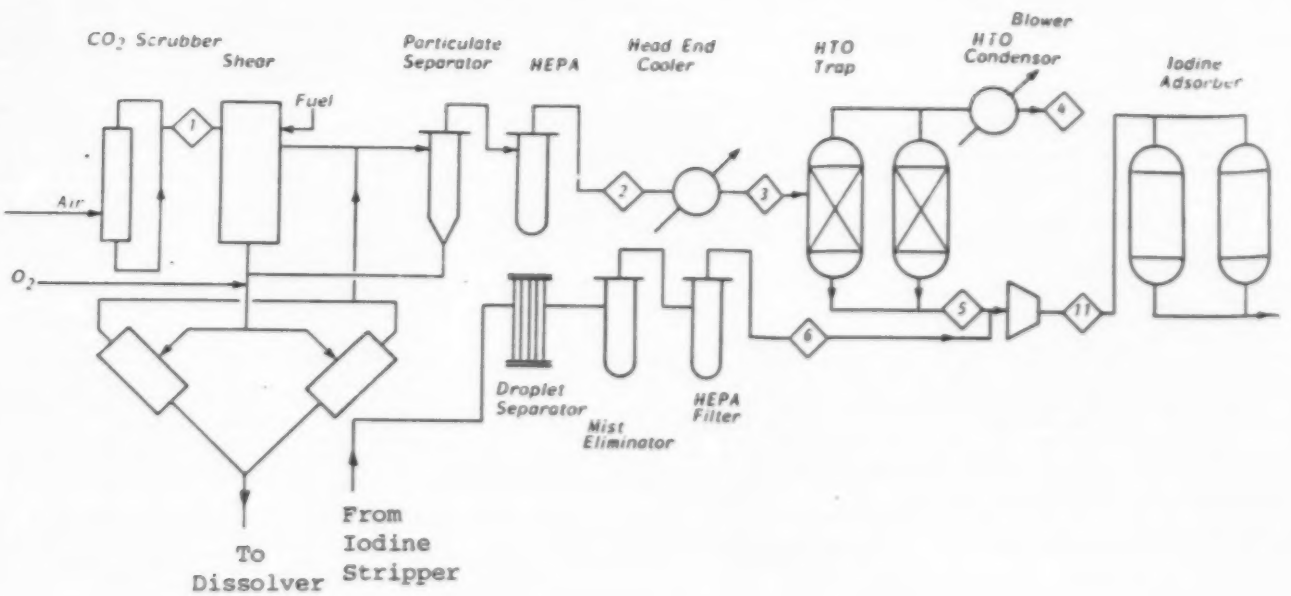
Air is used to carry the airborne radioactive nuclides; before its use the carbon dioxide content must be removed in order to avoid overloading of the carbon dioxide adsorbent bed unnecessarily. The carbon dioxide removal can be simply done by scrubbing with recycling caustic solution in a scrubber.

2.2 Head-End Off-Gas

About 500 Nm^3/d caustic treated CO_2 free air introduced into the chopping glove box goes with chopped fuel into voloxidizers. The oxygen stream, 235 Nm^3/d, is also introduced simultaneously to the voloxidizer to oxidize UO_2 to UO_3. The same amount of air, about 500 Nm^3/d, carries particulates into the particulate separator.

The tritium will evolve from the voloxidizer as HTO vapor (and also present as T_2O and DTO), with less than 0.1% as HT. The other fission gases (I-129, C-14, Kr-85 and Xe) are also released from the spent fuel during voloxidation. The off-gas from the voloxidizers also joins the stream. This combined stream forms the head-end off-gas (HOG) for further treatments.

As shown in the following sketch the HOG enters firstly into the mechanical particulate separator then to the HEPA filter. The stream 2 which comes out from the filter train will be cooled down before the trapping of HTO. After HTO is trapped the tritium free stream 5 is then combined with DOG.

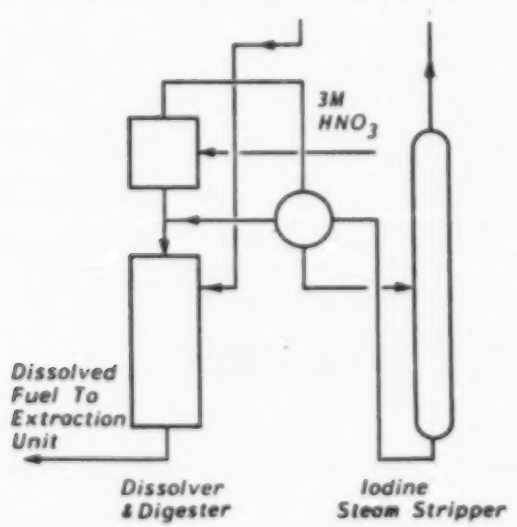


2.3 Dissolver Off-Gas

The voloxidized fuel, in UO_3 form is dissolved in nitric acid causing the gaseous radioisotopes remaining in the fuel to be released. The operating mode of the dissolvers is identical to that described earlier for the direct dissolution option (Appendix A). The DOG is then sent to the iodine stripper to stream strip the I-129 from the nitric acid vapour. Since uranium is already in the form of U(VI) before entering into dissolver no NO_x would be generated during the dissolution. Then, the DOG stream is passed to the droplet and mist separator and is to be combined with the HOG for further treatment.

Following the methodology established in Appendix A, for direct dissolution, the sketch and process streams are calculated and summarized in the table following.

Stream No.	①	②	③	④	⑤	⑥
Pressure, kPaa	90	90	85	101	80	80
Temperature, °C	25	600	40	25	40	30
Flow, K.Mol/Day						
Ar	4.0283 E-1	2.0142 E-1	2.0142 E-1		2.0142 E-1	2.0142 E-1
N_2	3.3641 E+1	1.6822 E+1	1.6822 E+1		1.6822 E+1	1.6822 E+1
O_2	9.0856 E0	4.5428 E0	4.5428 E0		4.5428 E0	4.5428 E0
H_2O	1.4015 E0	7.0075 E-1	7.0075 E-1	7.003 E-1	4.4587 E-4	5.210 E-1
Kr-85	-	4.6386 E-3	4.6386 E-3		4.6386 E-3	-
Xe	-	4.9353 E-2	4.9353 E-2		4.9353 E-2	-
I-129	-	1.0805 E-3	1.0805 E-3		1.0805 E-3	1.0805 E-3
14-CO_2	-	8.480 E-8	8.480 E-8		8.480 E-8	-
HTO	-	2.352 E-5	2.352 E-5	2.3513 E-5	7.4836 E-8	-
Total			4.4587 E+1			



2.4 Off-Gas Clean-up Train

The combined off-gas consisting of components, iodine-129, carbon-14 and noble gases is similar to that from direct dissolution process. The treatment processes are almost identical to that described in Appendix A except slight variations in quantities. The differences are shown earlier in Figure 4 of the main text of this report.

DISTRIBUTION

Dr. D. Mills	Director of Research
Mr. H.N. Isaac	Design & Development, H10 A27
Mr. T.J. Carter	Design & Development, H10 A25
Mr. J. Li	Design & Development, H10 A23
Dr. S.J. Naqvi *	Design & Development, H10 A17
Dr. C. Frost (3)	Design & Development, H10 D22
Mr. R.A. McEachran	Design & Development, H10 A21
Mr. R.E. Heathcock	Design & Development, H10 A22
Dr. S.H. Hawthorne	Chemical Research
Dr. B.R. Nott	Chemical Research
Mr. A.S. Williamson	Chemical Research
Dr. Y.V. Nguyen	Chemical Research
Dr. S-D. Chang	Chemical Research

Public Reference Centre
Editorial Section (2)
Office Copies (3)
Extra Copies (3)

* Extra copies for transmittal by C.R. Frost to:

Dr. D.R. McLean	Atomic Energy of Canada Limited, WNRE
Dr. T.S. Sridhar	Atomic Energy of Canada Limited, WNRE